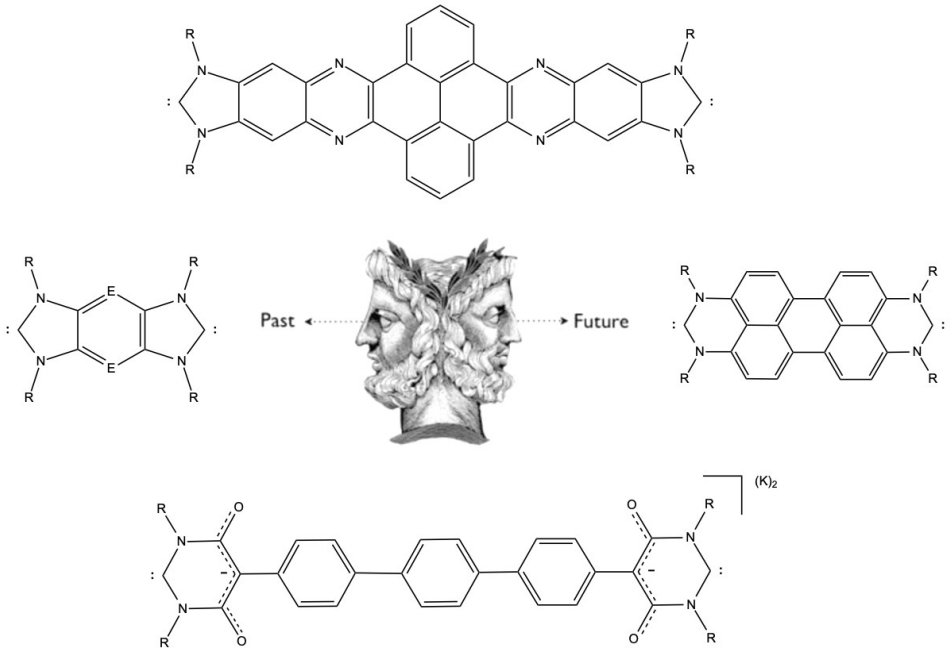
A review in Janus-type bis-NHC ligands



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Research Group: Organometallic Chemistry and Homogeneus Catalysis

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Acknowledgements

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I would also like to thank my classmates and friends, with whom I shared this 5 years of career, hours inside and outside the university, with whom I shared joys and sorrows, and definitely with whom I shared some of the, probably, best years of my life.

And finally, I would like to thank to my family for all their support throughout all this years, for having made it possible for me to become who I am now.

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Nomenclature and abbreviations:

NHC	N-heterocyclic carbene	**Et_3N**	Triethylamine
HCO_2H	Formic acid	**Dipp**	2,6-Diisopropylphenyl
RX	Alkyl halide	**CuI**	Cooper (I) Iodide
RNH_2	Primary amine	**Cs_2CO_3**	Cesium Carbonate
***t*BuONa**	Sodium tert-butoxide	**$BaCl{\cdot}H_2O$**	Hydrated Barium
$Pd(OAc)_2$	Palladium (II) acetate	**HCl**	Hydrochloric acid
Cy	Cyclohexyl	**MeOH**	Methanol
$HC(OEt)_3$	Triethyl orthoformate	**PCl_5**	Phosphorus pentachloride
HBF_4	Tetrafluoroboric acid	**K_3PO_4**	Potassium phosphate
Pd/C	Palladium on carbon catalyst	**XPhos Pd G3**	3rd generation Buchwald precatalyst
EtOH	Ethanol	**Ph_3PAuCl**	Chloro(triphenylphosphine) gold (I)
LDA	Lithium diisopropylamine	**$Ph_3PAgOTf$**	Triflate(triphenylphosphine) silver
cod	1,5-Cyclooctadiene	**KHMDS**	Potassium bis(trimethylsilyl)amide
$[RhCl(cod)]_2$	Cyclooctadiene rhodium chloride dimer	**nBuLi**	n-Butyllithium
tBuOK	Potassium tert-butoxide	**$PhPCl_2$**	P,P-Dichlorophenylphosphine
r. t.	Room temperature	**ditz**	1,2,4-Triazole-3,5-dylidene
CH_2Cl_2	Dichloromethane	**THF**	Tetrahydrofuran
NaBr	Sodium bromide	**DMSO**	Dimethyl sulfoxide
MeOTf	Methyl triflate	**TAP**	3,4,9,10-Tetraaminoperylene
TPHDP	tetrakis(phosphinomethyl)-1,2,3,8,9,10-hexahydrobenzo-[1,2,3-*gh:4,5,6-g'h'*] diperimidine derivative	**IPr·HCl**	1,3-Bis(2,6-diisopropylpheyl)imidazolium chloride

***i*Pr**	*iso*-Propyl	**Ph**	Phenyl
Δ	Reflux	**DMF**	*N*,*N*-Dimethylformamide
AgOAc	Silver acetate	**CH_3CN**	Acetonitrile
TIP	Tetrakis(iminopyracene)	**HPR_2**	Secondary phosphine
***t*Amyl**	*tert*-Amyl alcohol		

1 Introduction

From the late 1980s to the early 1990s, Bertrand, Arduengo and their co-workers synthesized and isolated stable nucleophilic carbenes[1–3]. Since then, N-heterocyclic carbene ligands (from now on NHCs) have been elevated from mere laboratory curiosities to became one of the most powerful tools in organic and inorganic chemistry, with numerous applications in commercially important synthetic processes.

A carbene is a neutral compound that contains a divalent carbon atom with a six-electron valence shell. Due to their incomplete electron octet and the coordinative unsaturation, free carbenes are unstable and were considered as highly reactive intermediates for organic transformations.

In NHCs, the carbene is stabilized by at least one nitrogen atom within the ring structure[4]. NHCs have been used as ligands in organometallic chemistry to replace the electron-rich and almost ubiquitous phosphine ligands. The chemistry of NHCs has being focused in the development of efficient organometallic catalysts for classic organic reactions, ascending from mere laboratory curiosities to compounds of enormous practical significance as more and more of the rich chemistry of these compounds have been studied and exploited.

Among NHCs, poly-NHCs have attracted great interest since they allow the preparation of organometallic complexes with very diverse topologies. Indeed, a wide set of complexes with bis-, tris-, and tetra-NHCs that can act as bichelating, pincer, tripodal, or bridging ligands is available nowadays.

Bis-NHCs are by far the most abundant poly-NHC ligands and the majority of them are designed to bind to one metal in a chelating way, as a result of their high entropic stability due to the formation of the ring once coordinated to the metallic center. Still, designing non-chelating-NHCs ligands have its own interest, since these ligands can provide homodimetallic and heterodimetallic complexes with advantages for catalysis purposes.

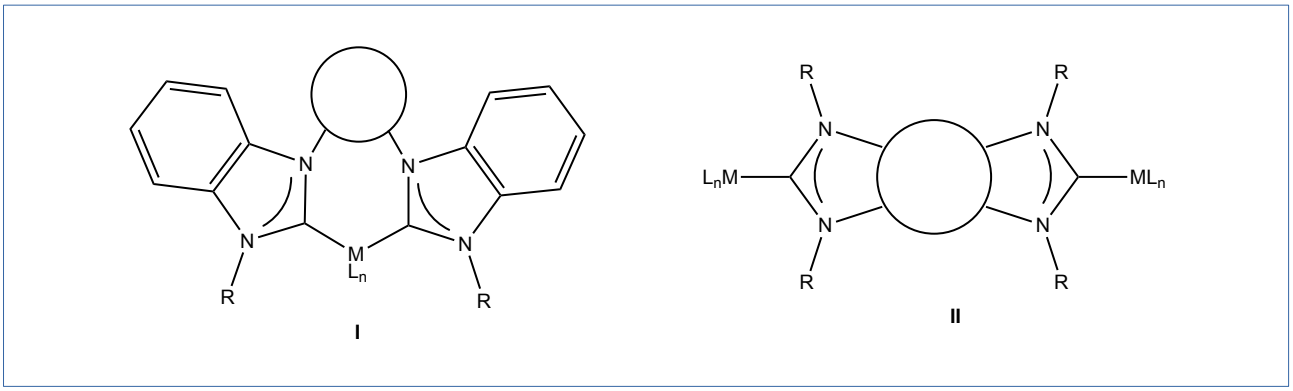


Figure 1. *Bis-NHCs coordinating to metallic centers in a chelating way (**I**) and acting as a bridge (**II**)*

In this project, we will discuss different bis-NHCs that are capable to bind in a facially-opposed disposition, called Janus-type ligands. This name comes from the Roman god Janus, who had two faces facing opposite directions, one said to be looking to the past, and the other to the future (Figure 2).

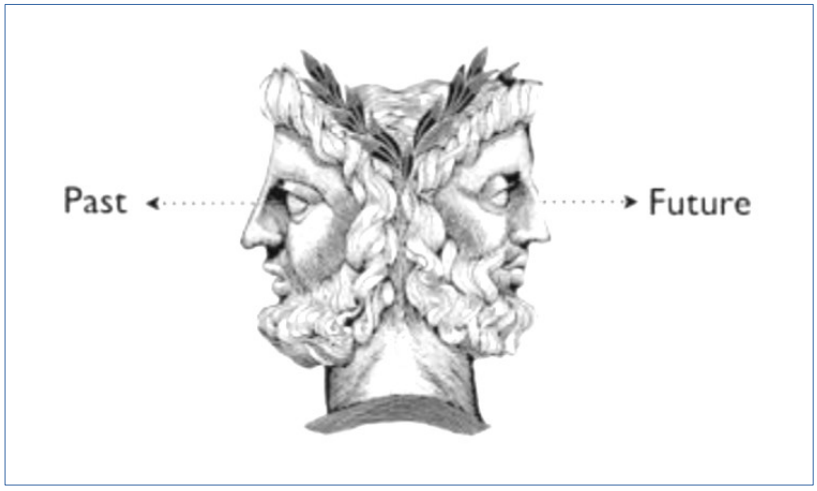


Figure 2. *Representation of the Roman god Janus*

In a similar way, Janus-type ligands bind to two metallic centers in a facially opposed disposition, as a result of its overall rigid topology that forces a bridge between them, forming dimetallic complexes.

This architecture has many modular features[5], including the linker between the carbene moieties, pendant substituents on the nitrogen atoms, heteroatoms… Therefore making possible to tune the structural, electronic, mechanical and physical characteristics of the resulting organometallic material, with simple variations of the starting material (Figure 3).

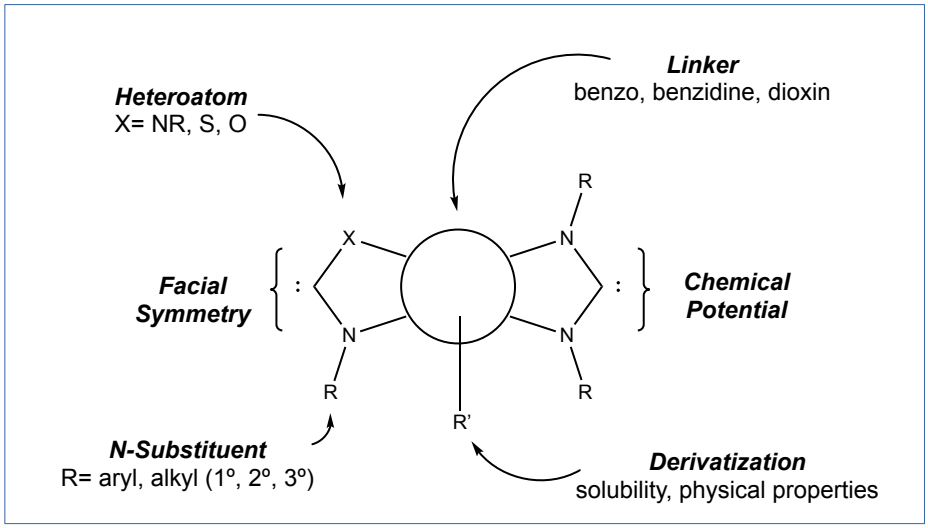


Figure 3. *Modular features of a Janus-type bis-NHC structure*

2 Classification

The first reported Janus-type bis-NHC ligand was the 1,2,4-triazole-3,5-dylidene **A** (so called ditz ligand)[6]. Ligand **A** was first used as a building block for an organometallic Ag(I)-based polymer by Bertrand and co-workers in early 1997 (Scheme 1) instead of a ligand in organometallic complexes with catalytic purposes[6].

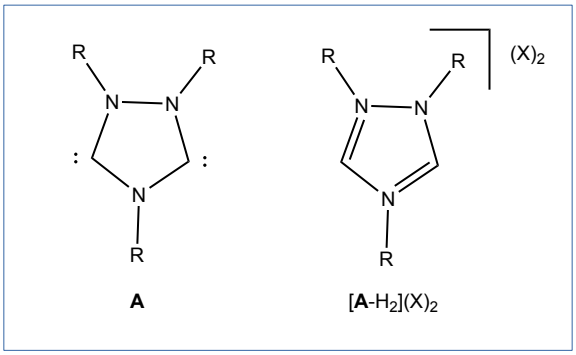
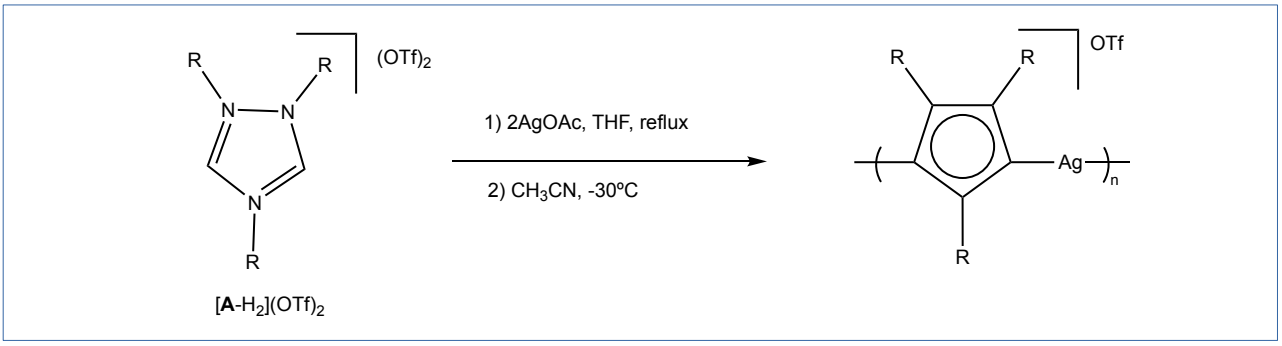


Figure 4. *Ditz and its precursor*



Scheme 1. *Synthesis of an organometallic polymer based on ditz ligand starting from* $[\mathbf{A}\text{-}H_2](OTf)_2$

Ditz ligand is very important within the family of Janus-type bis-NHC ligands since it has shown the ability to coordinate to two different metallic centers, which can be very interesting from the catalytic point of view. This will be discussed in detail in section 3 of this review project.

The rest of Janus-type bis-NHCs discussed in this review, consist in more than one aromatic ring, having a core that links the two carbene centers. Attending to the linker between the two NHC moieties and their features, we have decided to classify Janus-type bis-NHCs in: aromatic-linked (**a**), dianionic systems (**b**) and redox-center-linked (**c**). Figure 5 depicts one example of each of these categories.

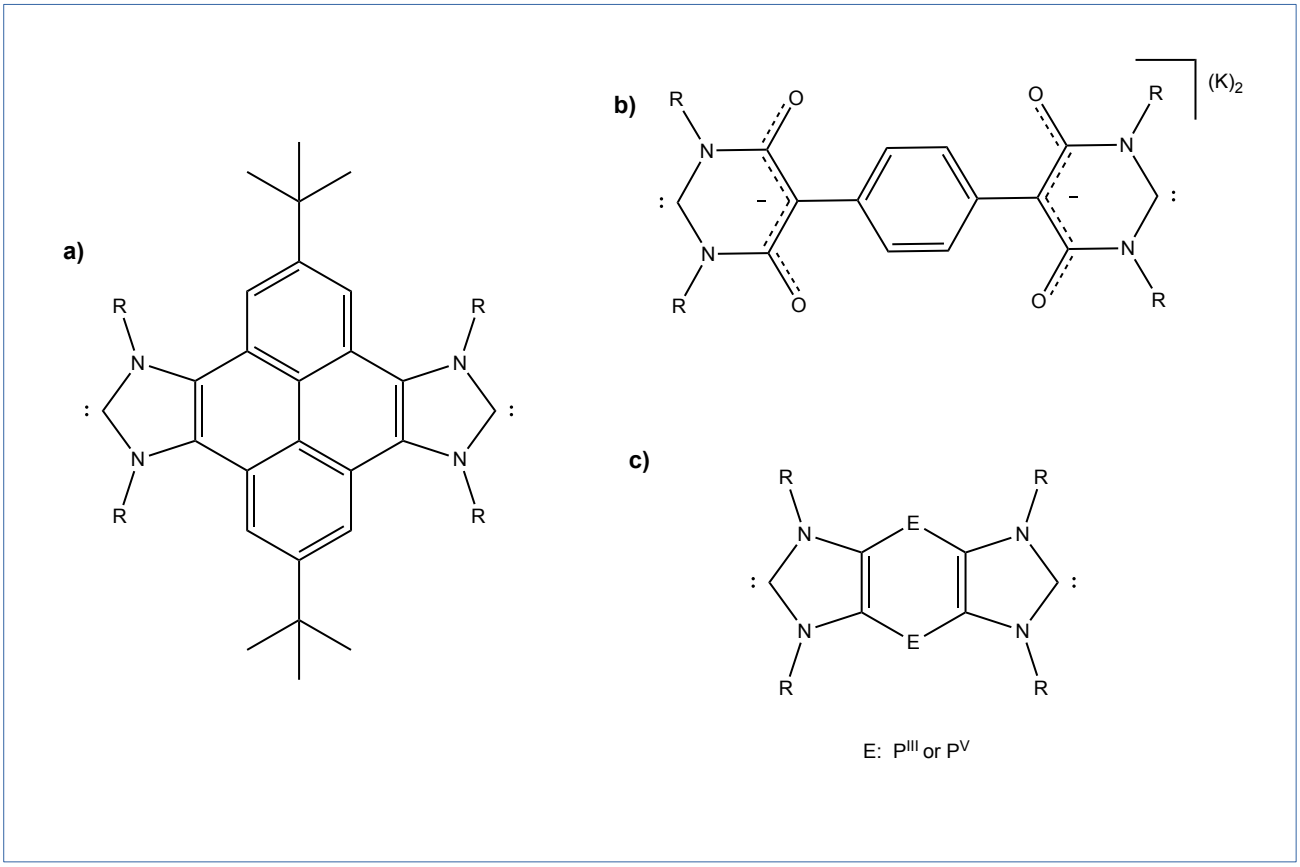


Figure 5. *Different types of Janus-type ligands*

2.1 Aromatic-linked Janus-type bis-NHCs

The main characteristic of this group is that the carbene moieties are linked by an aromatic or polyaromatic system. Upon coordination to a metal center, the rigidity of the aromatic system in these ligands provides a constant intermetallic distance within the organometallic complex, as well as rigidity, partially preventing twirls and bends.

Figure 6 depicts some of the most representative examples of this class of ligands, based in aromatic systems such as bencene (**B**), pyracene (**C**), pyrene (**D**), quinoxalinophenanthrophenazine (**E**) and perylene (**F**).

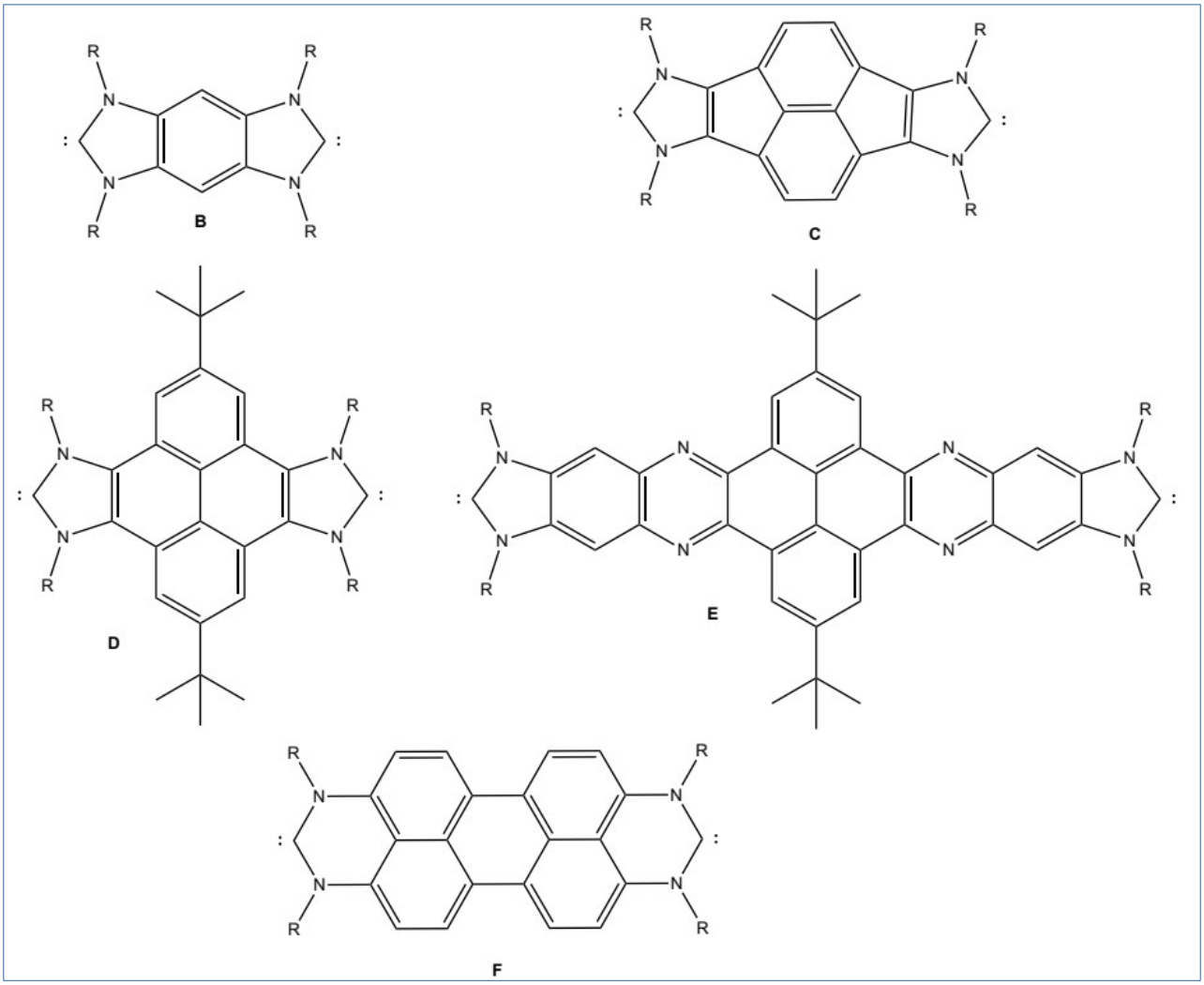
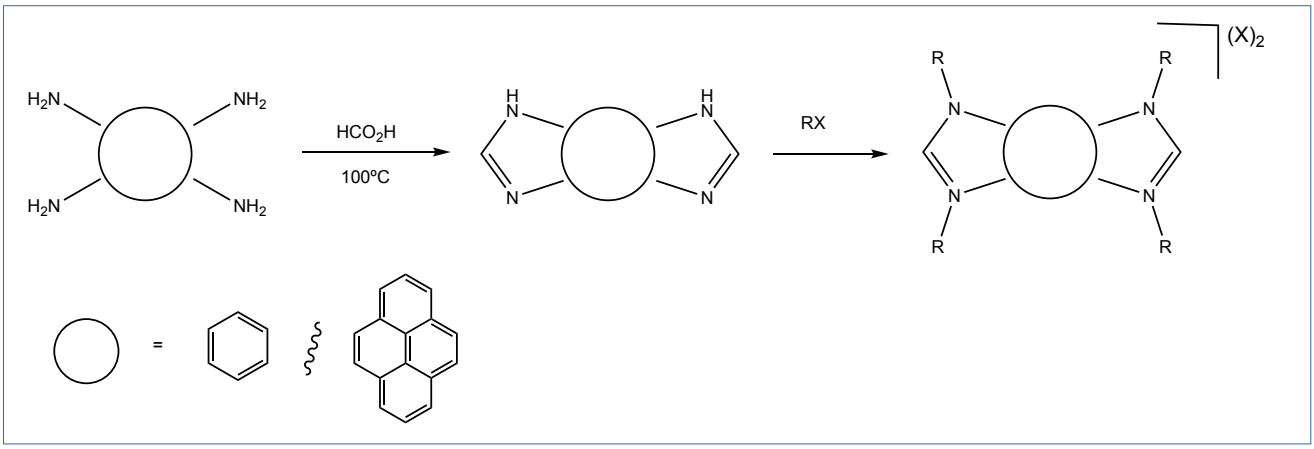


Figure 6. *Examples of aromatic-linked Janus-type bis-NHCs*

2.1.1 Synthesis of the precursors of the ligands

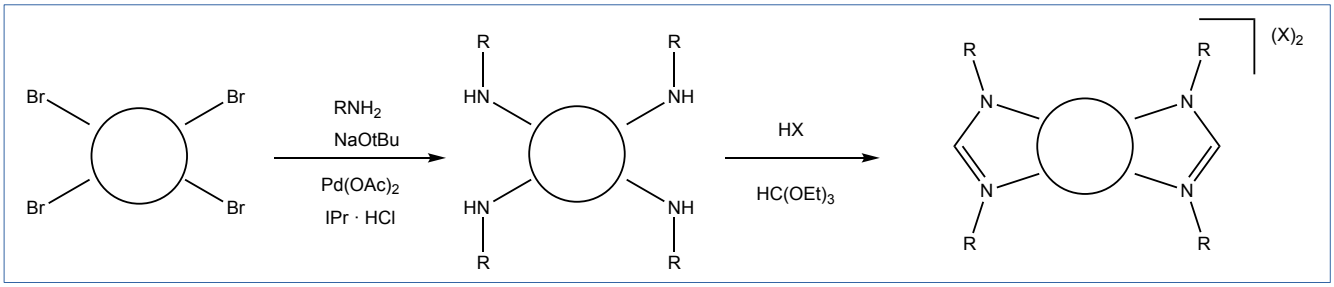
As we will indicate throughout the text, imidazolium salts are the most commonly employed precursors for NHC ligands. The precursors of these ligands were synthesized following different synthetic routes. One of them is the cyclation/alkylation synthetic protocol depicted in Scheme 2, first proposed by Prof. Bielawski and co-workers[5].



Scheme 2. *Synthesis of a bis(imidazolium) salts from tetraamino arenes via cyclation/ alkylation*

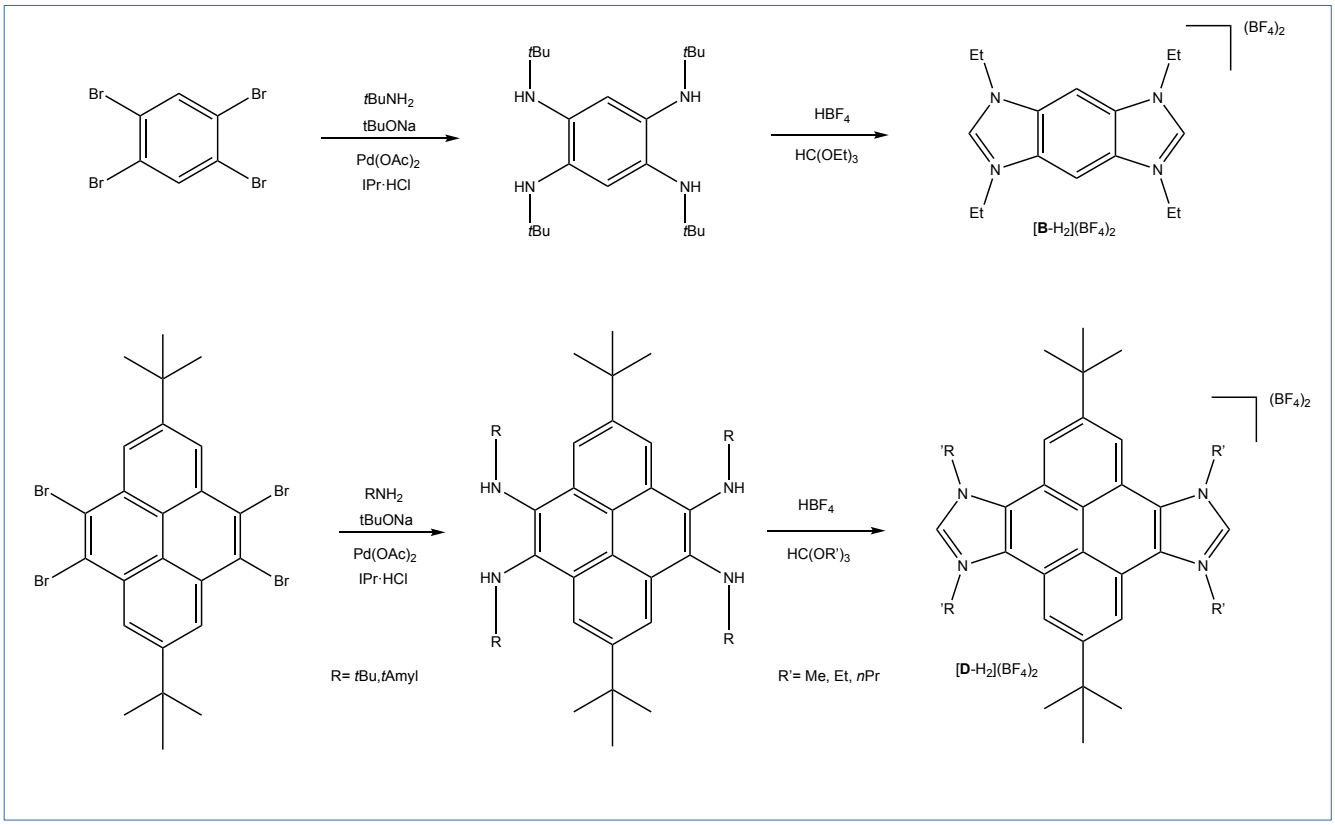
As shown in Scheme 2, cyclization of tetraaminoarenes with formic acid produces the corresponding annulated bis(imidazoles) that can be alkylated with primary alkyl halides to afford their corresponding bis(imidazolium) salts.

However, this protocol has the limitation that neither N-aryl nor bulky N-aryl groups can be incorporated due to the impossibility of their electrophilic precursors to carry out S_N2-type reactions. This issue can be solved using a different synthesis path, such as the synthesis via four-fold aryl-amination/cyclization, described by Prof. Bielawski and co-workers in 2005[7]. As indicated in Scheme 3, this reaction consists in the coupling of bulky amines with a tetrachloro or tetrabromo-substituted aromatic core, catalyzed by $Pd(OAc)_2$ and 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (IPr·HCl), followed by a formylative cyclization with triethylorthoformate under acidic conditions, to provide the corresponding bis(imidazolium) salt.



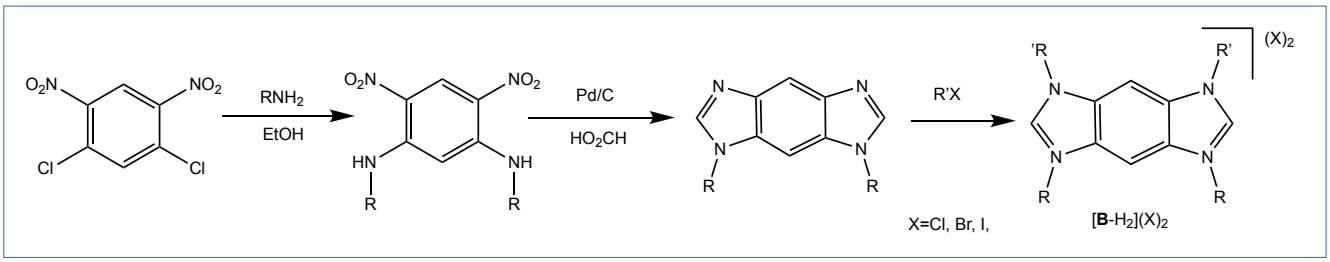
Scheme 3. *Synthesis of bis(imidazolium) salt via four-fold aryl amination/cyclization*

This path has been used specifically in the synthesis of salts [**B**-H_2]$(BF_4)_2$ and [**D**-H_2]$(BF_4)_2$ which are the precursors of ligands **B** and **D**, respectively. These salts were described by Profs. Bielawski and Peris, respectively[7,8] (Scheme 4).



Scheme 4. *Examples of four-fold amination/cyclization*

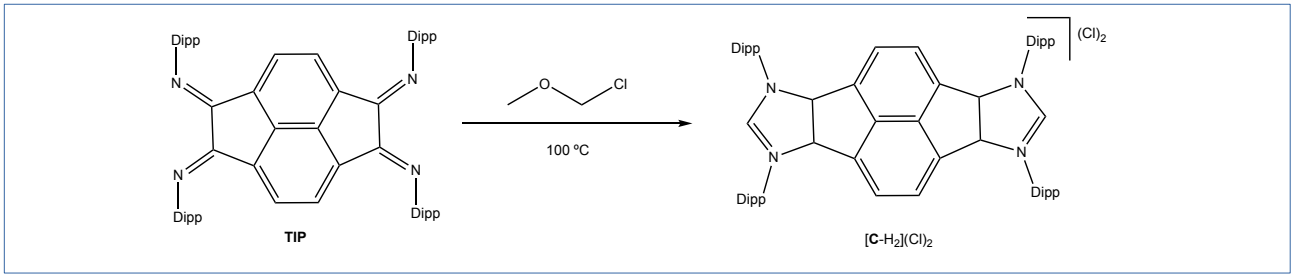
The desymmetrized version of the salt [**B**-H_2]$(BF_4)_2$ was prepared following a different protocol, illustrated in Scheme 5. The reaction involves a substitution of 1,5-dichloro-2,4-dinitrobenzene using a two-fold S_NAr-type reaction, followed by a reduction/cyclization. The key advantage of this procedure is the ability to incorporate a broad range of heteroatoms and the possibility to perform the entire reaction, from the commercial reagents to the final bis(imidazolium) salt, in ambient atmosphere with minimal purification protocols.



Scheme 5. *Synthesis of a desymmetrized bis(imidazolium) salt via double S_NAr protocol*

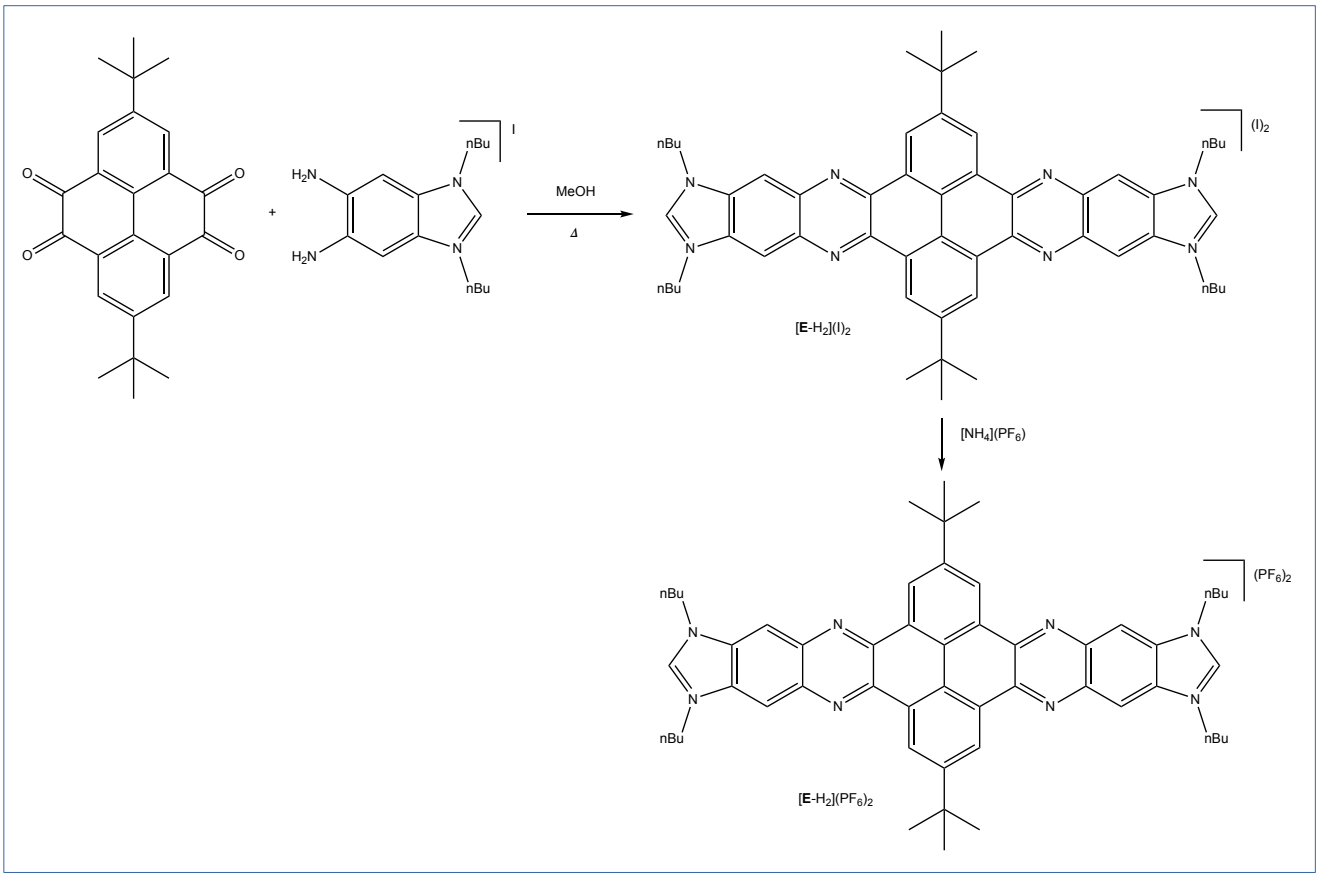
The precursors of ligands **C**, **E**, and **F**, were synthesized following specific protocols.

The precursor of salt **C**, namely [**C**-H_2]$(Cl)_2$, can be obtained by the bisannulation of tetrakis(iminopyracene) (TIP) with chloromethyl methyl ether, as showed by Profs. Peris and Alcarazo in 2012[9] (Scheme 6).



Scheme 6. *Synthesis of [**C**-H_2](Cl)$_2$ by bisannulation of TIP*

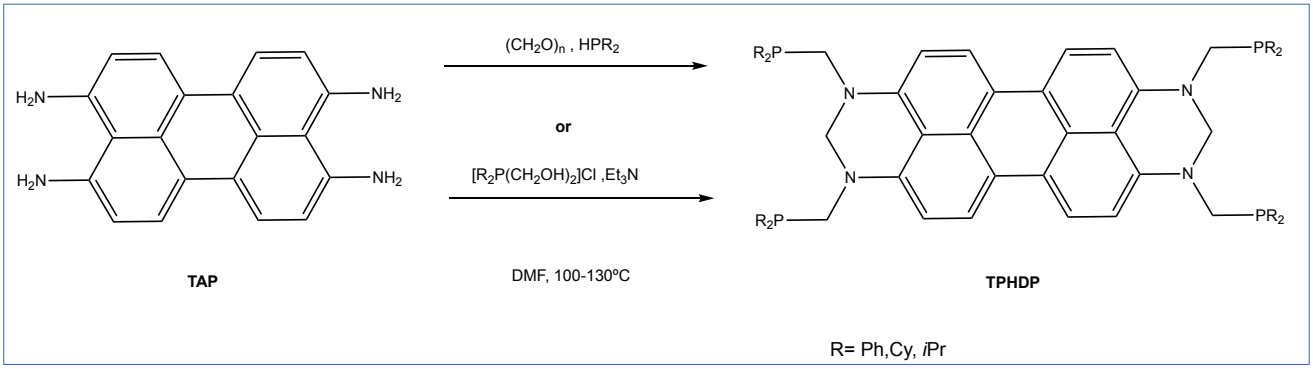
The precursor of ligand **E**, the longest ligand within this category, was synthesized by Profs. Peris and Poyatos in 2015[10]. This ligand is based on a quinoxalinophenanthrophenazine core, and its precursor can be obtained from the direct condensation of pyrene-4,5,9,10-tetraone with 1,3-dibutyl-5,6-diaminobenzimidazolium iodide in methanol, followed by an anion metathesis with [NH_4](PF_6) giving the corresponding hexafluorophosphate salt, as shown in Scheme 7.



Scheme 7. *Synthesis of [**E**-H_2](PF_6)$_2$ by direct condensation followed by anion methatesis*

The last ligand in this group, ligand **F**, differs from the rest by not having a bisimidazolium salt as a precursor. In this case, the precursor is a tetrakis(phosphinomethyl)-1,2,3,8,9,10-hexahydrobenzo-[1,2,3-*gh:4,5,6-g'h'*] diperimidine derivative (TPHDP from now on).

The synthesis of the precursor of ligand **F**, TPHDP, was described by Prof. Gade and co-workers in 2016[11]. It consisted in the direct reaction of 3,4,9,10-tetraaminoperylene (TAP) with either the corresponding phosphine and paraformaldehyde or with the phosphonium salt and triethylamine as base using *N,N*-dimethylformamide as solvent (Scheme 8).

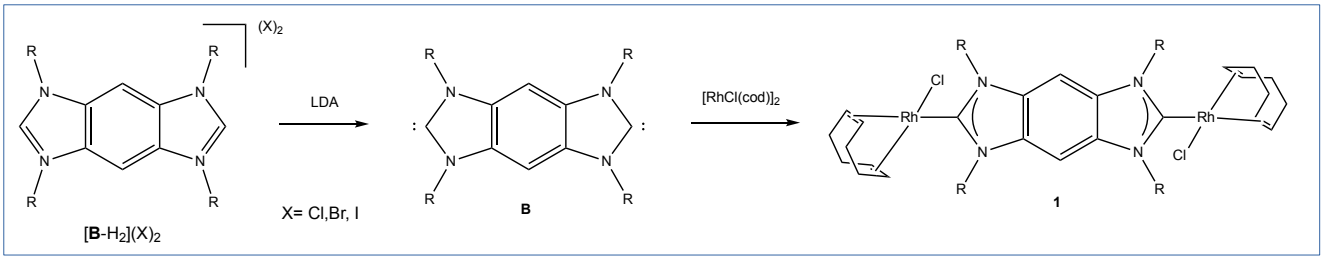


Scheme 8. *Synthesis of the precursor of* ***F*** *THPD from TAP*

2.1.2 Metal complexes and properties

With the ligand precursors in hand, the coordination to a metal center requires their previous activation that, for imidazolium salts, implies a deprotonation with a base.

These ligands have been coordinated to a wide range of metal centers. The first that we are going to discuss and the first example of linearly opposed coordination of NHCs is the bimetallic complex **1** synthesized by Prof. Bielawski and co-workers in 2006, starting from [**B**-H_2]$(X)_2$ precursor[5] (Scheme 9). First, the deprotonation is carried out by the reaction of the bis(imidazolium) salt with LDA, providing the free Janus-type ligand **B**, that is then reacted with $[RhCl(cod)]_2$, giving the desired bimetallic complex **1**.

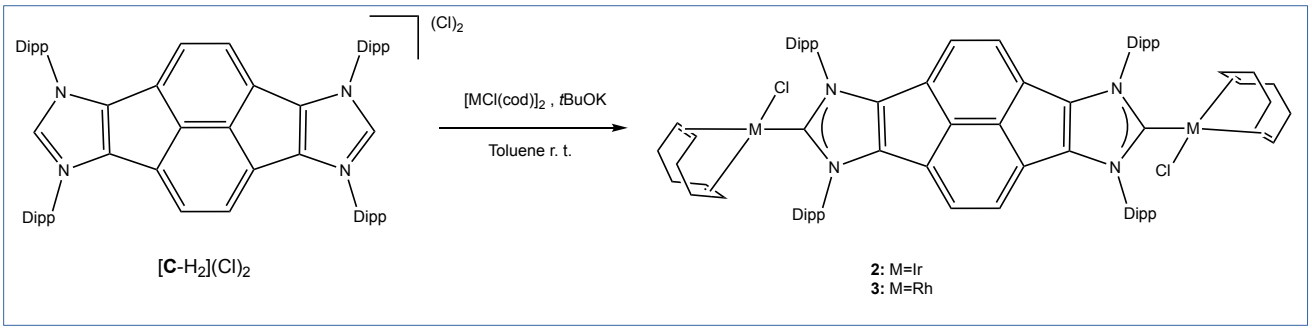


Scheme 9. *Synthesis of complex* ***1*** *from [****B****-H_2]$(X)_2$*

This linear bimetallic species have potential for use as monomers in further copolymerizations.

Complexes **2** and **3**, were synthesized by Profs. Peris and Alcarazo in 2012, by the coordination of ligand **C** to Ir(I) and Rh(I) as shown in Scheme 10[9].

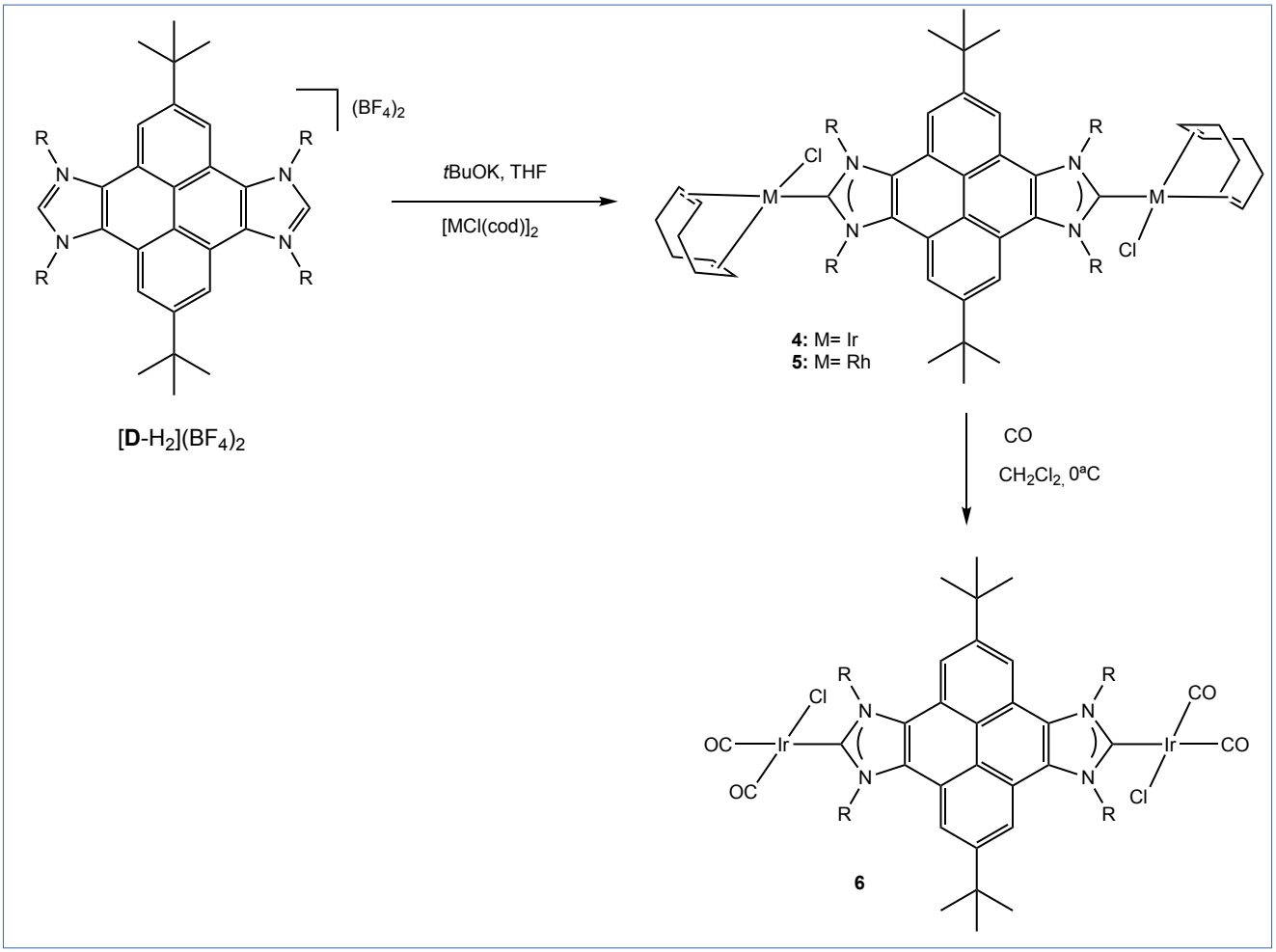
Despite the polyaromatic linker, these complexes consist in two essentially decoupled metal fragments, which may be used to coordinate different metallic centers without loosing its catalytic activity, in a cooperative way. These complexes displayed interesting electronic and structural features that make them potentially useful for the preparation of metalloorganic materials with catalytic applications.



[**C**-H_2]$(Cl)_2$

Scheme 10. *Synthesis of complexes **2** and **3** from [**C**-H_2]$(Cl)_2$*

Complexes containing ligand **D** were synthesized by Profs. Peris and Poyatos in 2014[8] with Ir and Rh and with Pd in 2019[12].

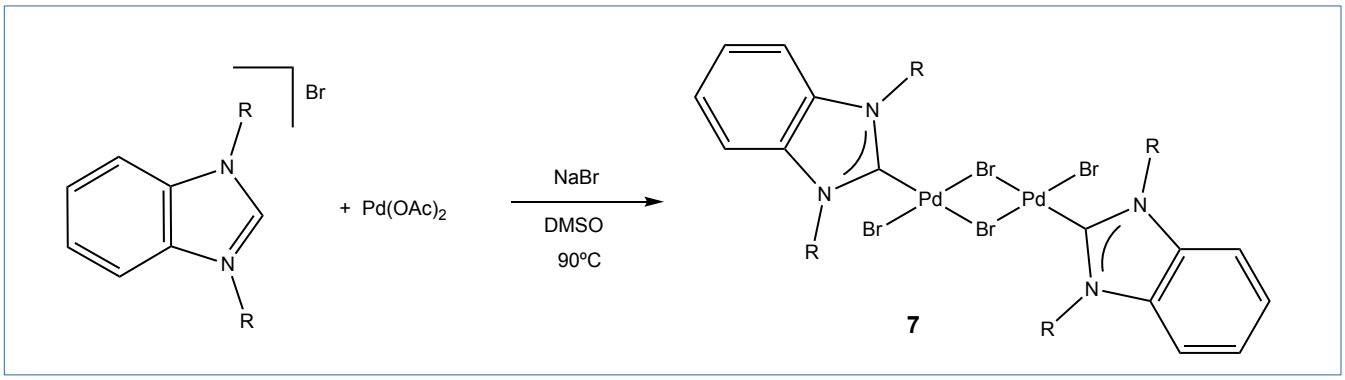


[**D**-H_2]$(BF_4)_2$

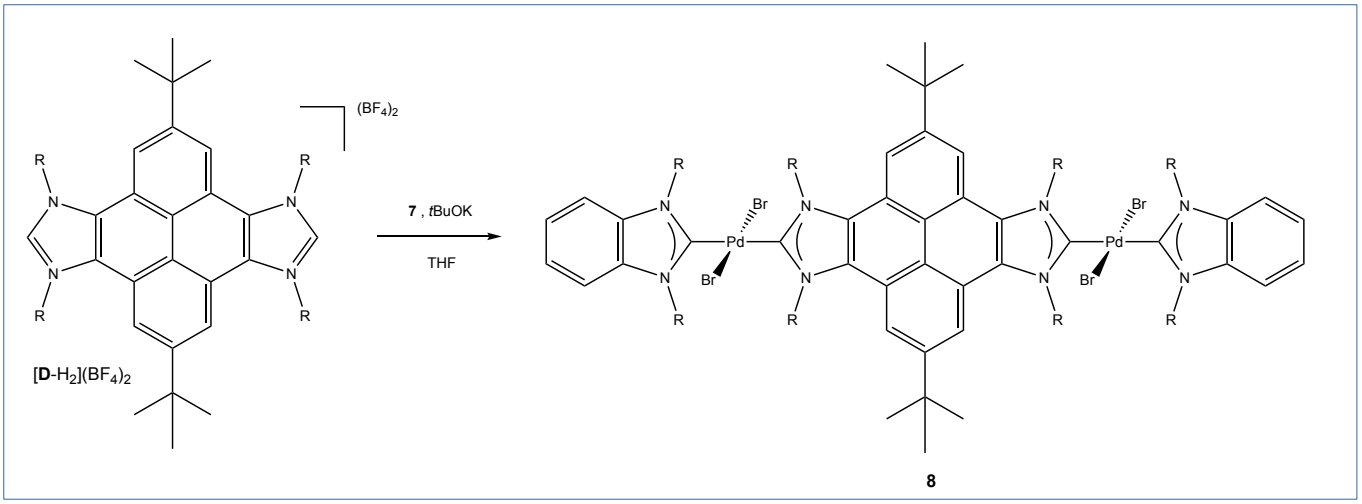
Scheme 11. *Synthesis of Ir and Rh pyrene-based complexes **4, 5** and **6** from the precursor salt [**D**-H_2]$(BF_4)_2$*

The procedure involves, the deprotonation of the corresponding bis(imidazolium) salt and subsequent coordination to the metallic center. The Ir(I) complex **4** was carbonilated in CH_2Cl_2 to obtain complex **6** (Scheme 11).

For the Pd(II) complex, it was necessary the previous synthesis of the dimetallic bridged complex **7** (Scheme 12), that was reacted afterwards with [**D**-H_2]$(BF_4)_2$ in the presence of *t*BuOK (Scheme 13).

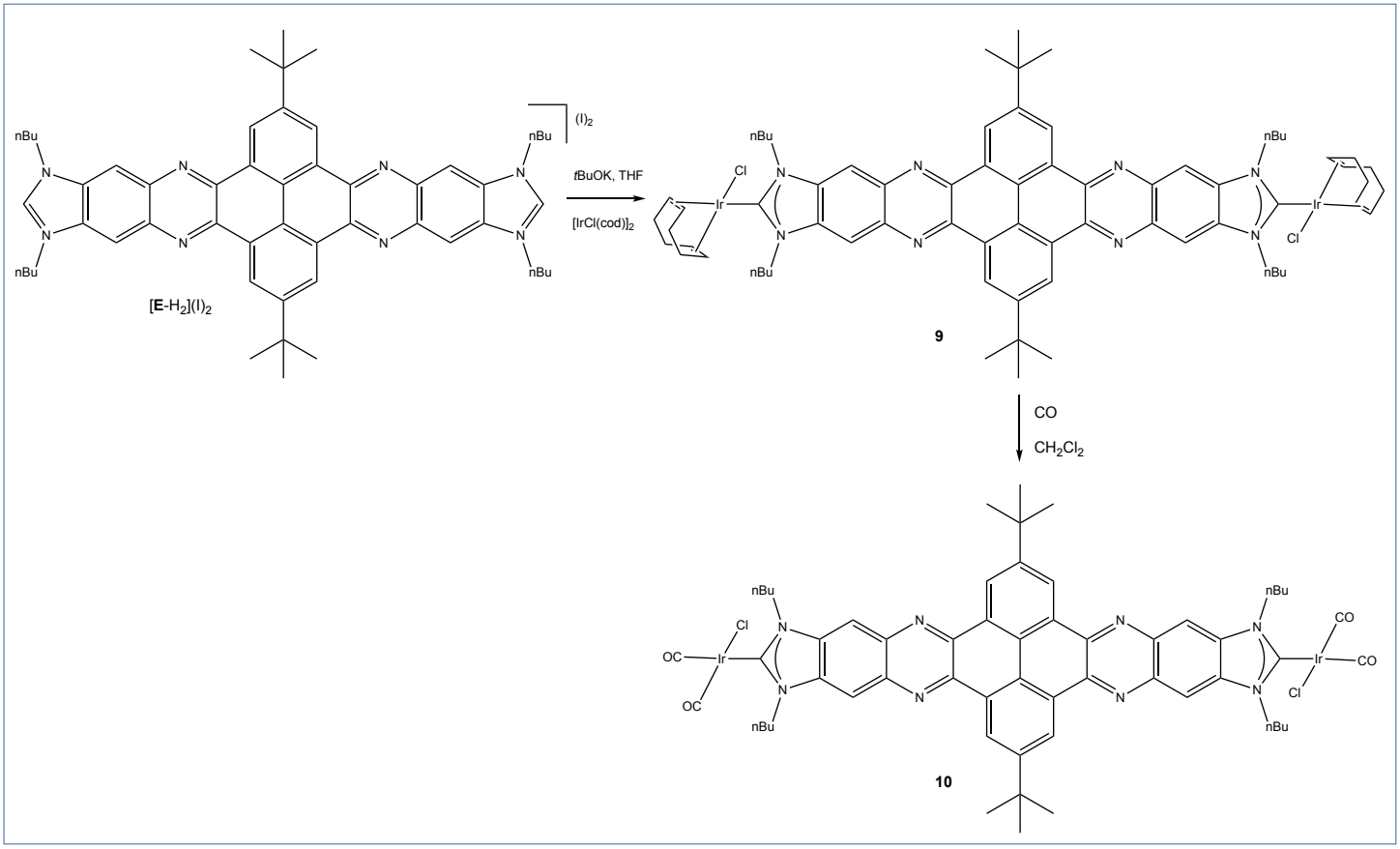


Scheme 12. *Synthesis of dimetallic Pd bridged complex **7***



Scheme 13. *Synthesis of complex **8** from dipalladium complex **7** and [**D**-H_2]$(BF_4)_2$*

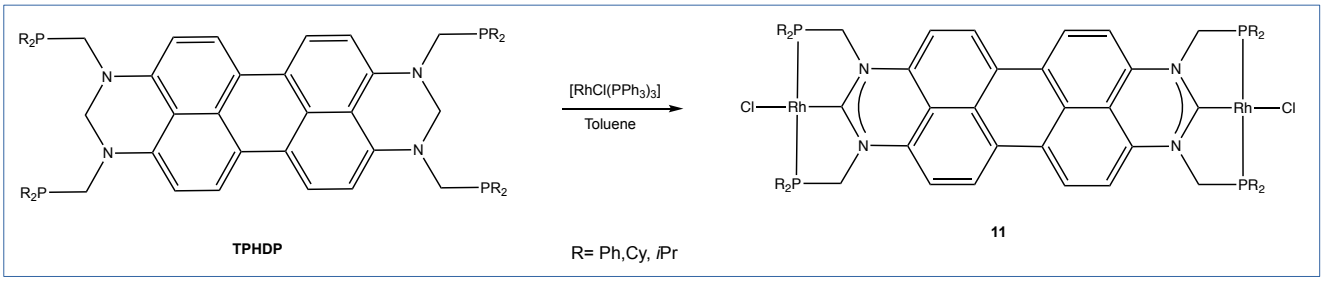
The largest complex of this group of aromatic-based Janus-type ligands was synthesized by Profs. Peris and Poyatos in 2015, coordinating ligand **E** to Ir(I)[10]. Once again, this synthetic path consists in the deprotonation of the bis(imidazolium) salt followed by the coordination to the metallic center giving complex **9** that could be carbonilated to complex **10** (Scheme 13).



Scheme 14. *Synthesis of complexes* ***9*** *and* ***10*** *from [**E**-H_2](I)$_2$*

These complexes have demonstrated to have π-stacking abilities and can be regarded as potential building blocks of supramolecular structures, such as squares or cages.

The precursor of ligand **F**, THPDP, can be reacted with [RhCl(PPh_3)$_3$] in toluene in order to obtain complex **11**. This complex differs from the rest because the coordination with the metallic center is carried out by a ditopic PCP pincer, as shown by Prof. Gade and co-workers in 2016[11] (scheme 15).



Scheme 15. *Synthesis of complex* ***11*** *from TPHDP, precursor of* ***F***

As indicated earlier, in this case, the precursor is not a bis(imidazolium) salt, and suffers a double C-H activation in order to coordinate with the metallic center[13]. These complexes display high fluorescence quantum yields.

2.2 Dianionic Janus-type ligands

The main characteristic of this group is the overall negative charge of the ligand, making possible to form neutral complexes with monocationic metals, such as Au^+ or Ag^+. This double negative charge is a consequence of the double anionic functionalities within the heterocyclic backbone (Figure 7).

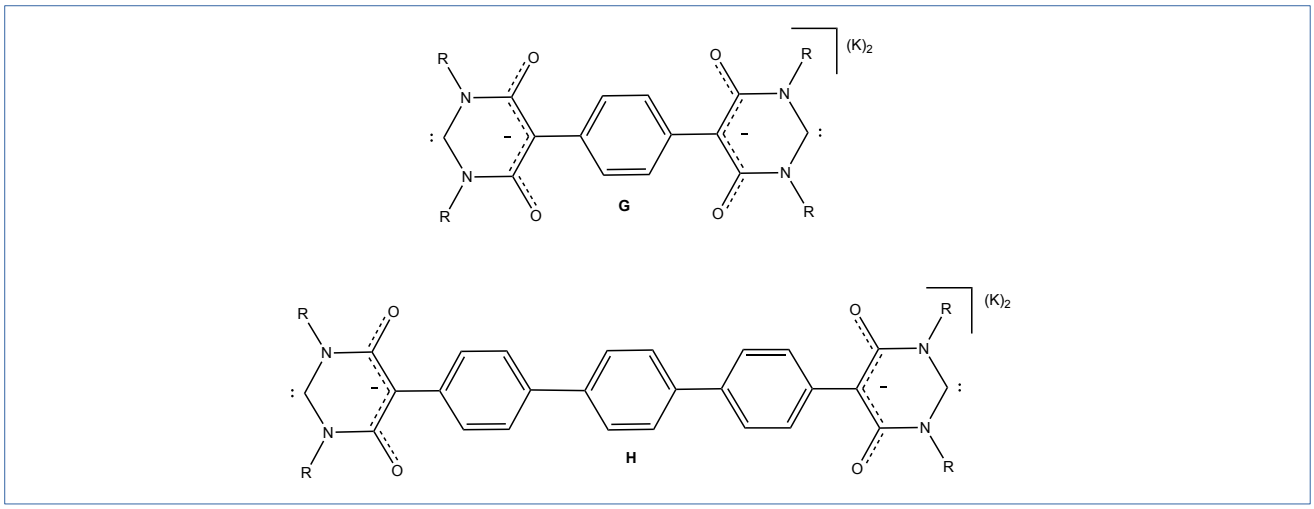
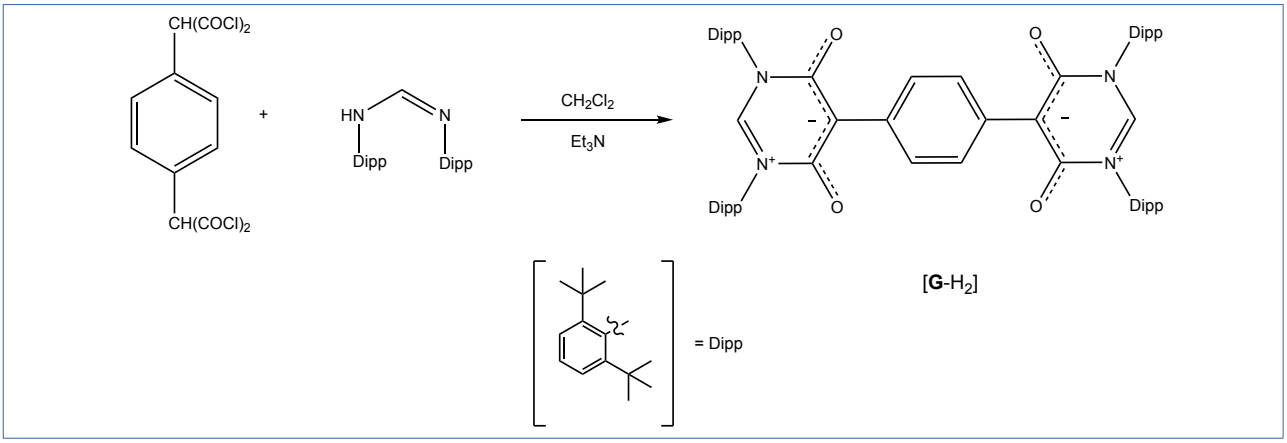


Figure 7. *Dianionic Janus-type ligands*

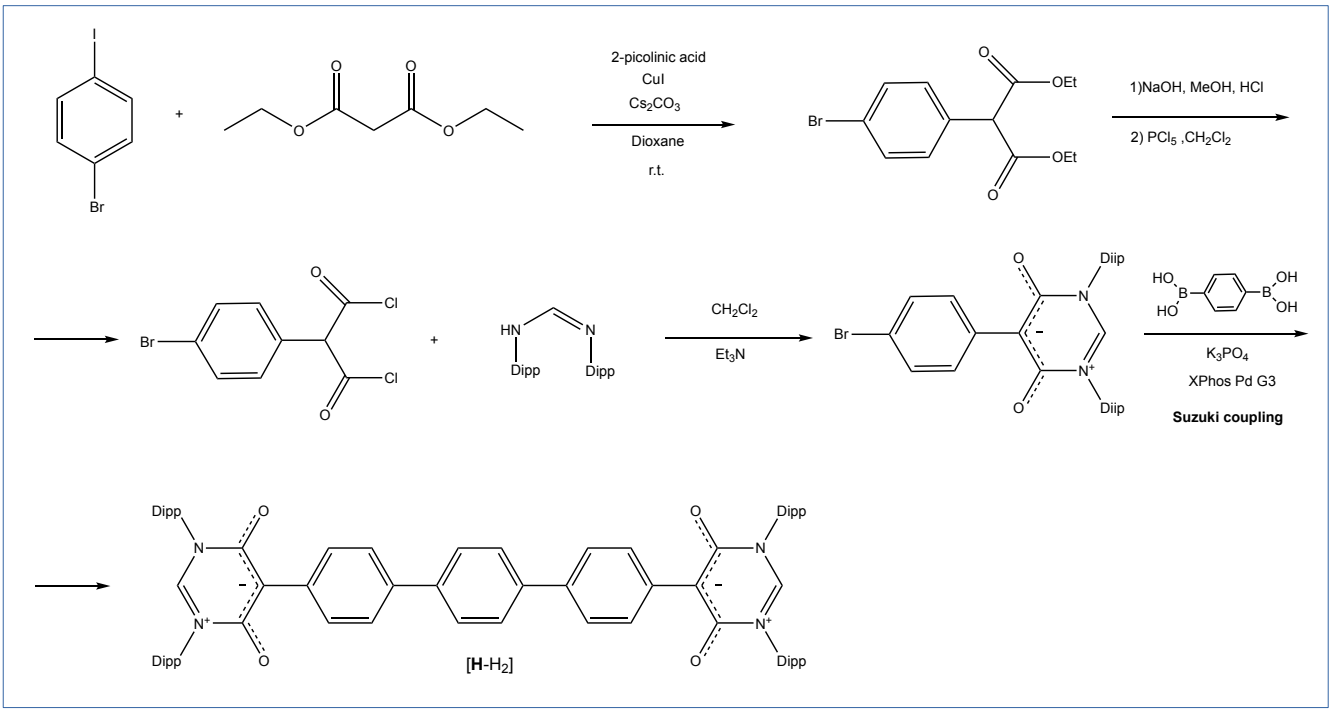
2.2.1 Synthesis of the precursors of the ligands

The synthesis of the precursors of these ligands, presented by Prof. Tapu and co-workers in 2014 and 2017, has some similarities, as expected observing the similar topography[14,15]. Still, compound [**G**-H_2] has a more direct synthesis starting with the coupling of 1,4-phenylenedimalonyl tetrachloride and N,N'-bis(2,6-di-isopropylphenyl)formamidine (Scheme 16).



Scheme 16. *Synthesis of the zwitterionic precursor [**G**-H_2]*

Compound [**H**-H_2] has an appreciably more challenging synthesis, as it needs some extra steps to build the larger core. First, diethyl 4-bromophenylmalonate is obtained through a copper-catalyzed α-arylation of diethyl malonate with 1-bromo-4-iodobenzene. Diethyl 4-bromophenylmalonate is then hydrolysed with NaOH in methanol, yielding 2-(4-bromophenyl)propanedioic acid. The conversion of this acid to its corresponding acyl halide is followed by a coupling with N,N'-bis(2,6-diisopropylphenyl)formamidine leading to the zwitterionic salt. Then, this salt was used as the starting material in a Suzuki coupling reaction with benzene-1,4-diboronic acid catalyzed with palladium yeilding the zwitterionic precursor [**H**-H_2] (Scheme 17).

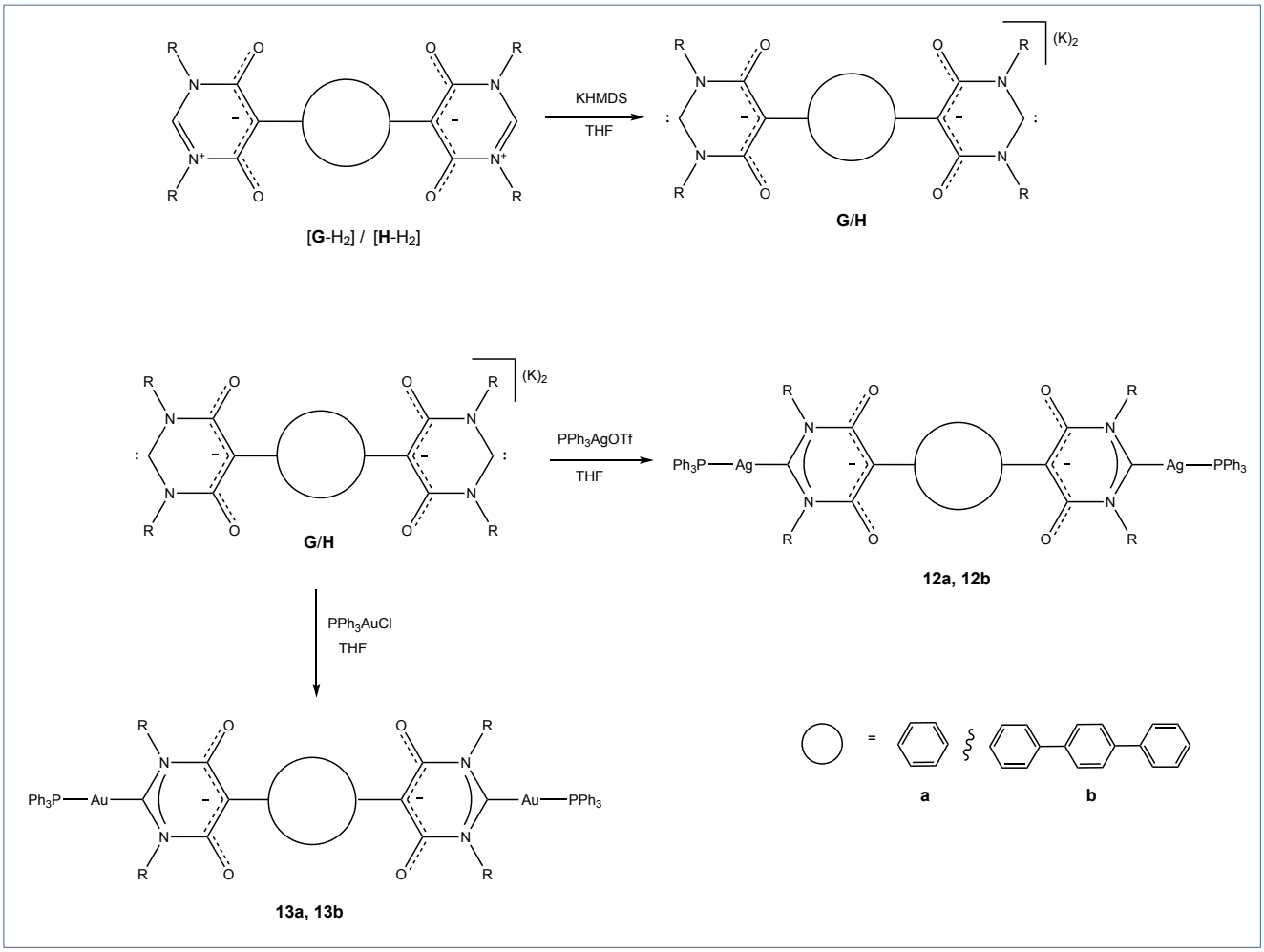


Scheme 17. *Synthesis of the zwitterionic precursor [**H**-H_2]*

2.2.2 Metallic complexes and properties

Once having the zwitterionic precursors in hand, the dimetallic complexes can be obtained by, upon deprotonation with a strong non-nucleophilic base, treating the carbene with the phosphine-stabilized precursors Ph_3PAuCl or $Ph_3PAgOTf$ (Scheme 18).

As we can see, these are neutral complexes formed with two monocationic metallic centers, such as Ag^+ and Au^+.



Scheme 18. *Synthesis of Au^+ and Ag^+ neutral complexes* ***12a, 12b, 13a*** *and* ***13b***

As a summary, the synthetic path of neutral organometallic complexes containing two monocationic metallic centers bridged with a dianionic Janus-type ligand consists in four major steps:

1) Preparation of a double acyl halide

2) Coupling with N,N'-bis(2,6-diisopropylphenyl)formamidine

3) Deprotonation using a strong non-nucleophilic base

4) Treatment with the phosphine-stabilized metallic precursor

2.3 Redox-center-linked Janus-type ligands

The main characteristic of the ligands of this category is the presence of a bridging heteroatom in the backbone, with the possibility to possess different oxidation states, enabling chemical diversity as well as providing a functional entity capable of being redox active and/or to possess different donor centers.

This group includes ligands depicted in Figure 8, in which we can see the heteroatom acting as a bridge in a flexible system such as **I** and in a rigid system as **J** and **K**.

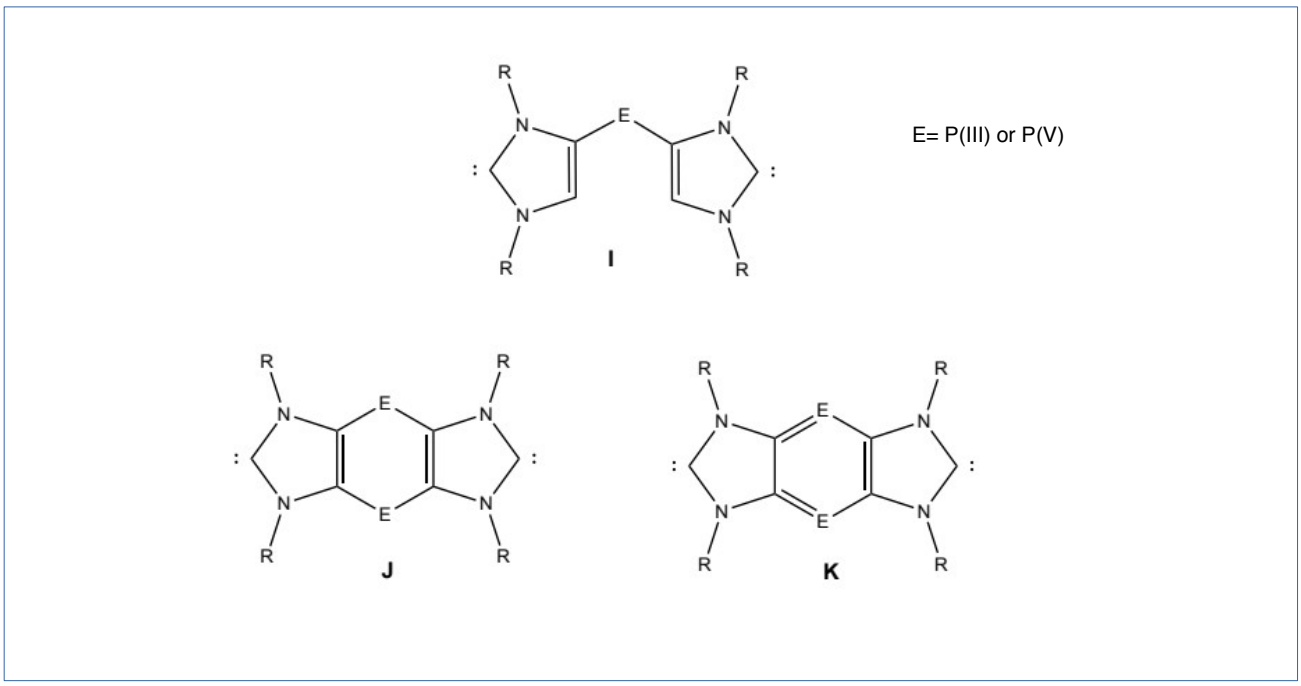
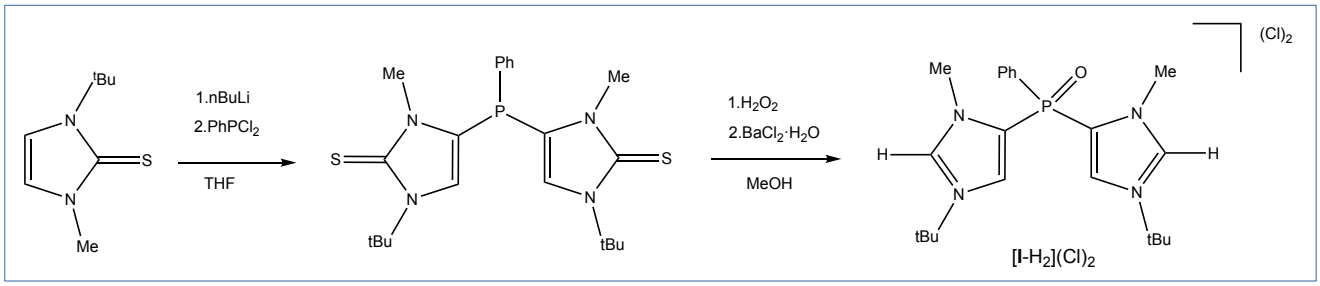


Figure 8. *Examples of redox active Janus-type ligands*

2.3.1 Synthesis of the precursors of the ligands

The synthetic path of [**I**-H_2]$(Cl)_2$ was presented by Prof. Streubel and co-workers in 2014[16]. It starts with the preparation of bis(imidazole-2-thion-4-yl)phosphane by the reaction of a imidazole-2-thione with nBuLi followed by $PhPCl_2$ in THF.

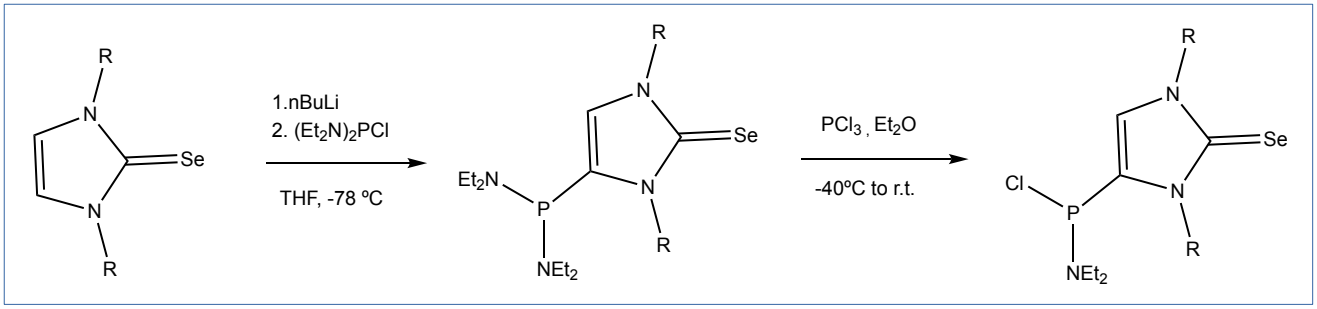
Once having bis(imidazole-2-thion-4-yl)phospane, [**I**-H_2]$(Cl)_2$ can be prepared by the reaction with 10 equivalents of H_2O_2 in a methanolic solution, providing the corresponding bis(imidazolium hydrogensulfate)salt, followed by $BaCl_2 \cdot H_2O$. With this process, P(III) can be oxidated to P(V) via an oxidative desulfuration[17] (Scheme 19).



Scheme 19. *Synthesis of [**I**-H_2]$(Cl)_2$ by an oxidative desulfuration*

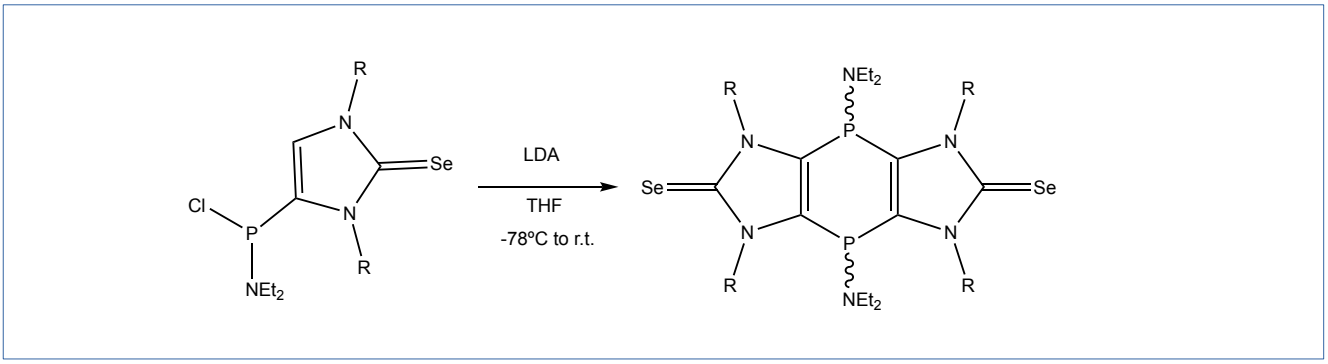
The synthesis of the rigid ring precursor is more complex, although it can be carried out with a similar starting material, the analogue imidazole-2-selenione. It starts with the reaction of the selenione with nBuLi and then with $(Et_2N)_2PCl$ in THF at -78ºC, obtaining the $P(NEt_2)_2$

functionality, making possible the access to a $P(Cl)NR_2$ functionality with the reaction with PCl_3 and Et_2O[18] (Scheme 20)



Scheme 20. *Synthesis of C^4 – substituted imidazole-2-seleniones*

After reacting the $P(Cl)NEt_2$ functionalized selenione with LDA in THF, the tricyclic compound could be obtained, as a mixture of the cis/trans stereoisomers (Scheme 21), in an analogue way as presented by Profs. Nyulászi and Streubel in 2017[19]. This product was also employed by Drs. Nylászi and Streubel to obtain the rigid redox active Janus-type ligand presented in 2020[20], its precursors and its organometallic complexes.



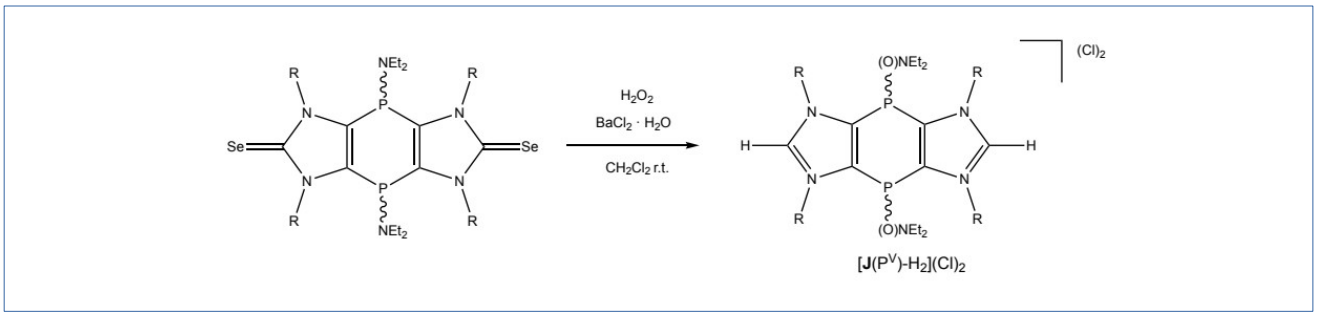
Scheme 21. *Synthesis of a tricyclic P-substitued derivative from a C^4-substitued imidazole-2-selenione*

Once having this starting material, the objective is to form the corresponding ligand precursors with the phosphorous atom in oxidation states +3 and +5.

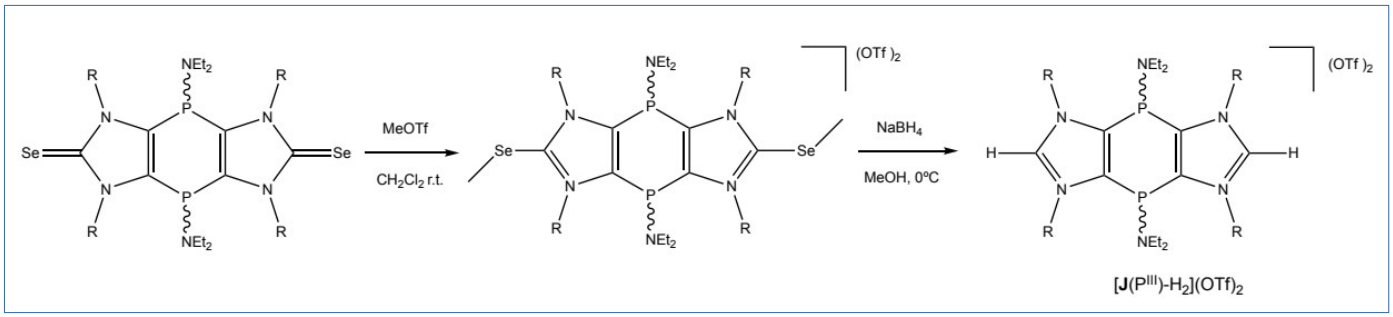
Since in the starting material the oxidation state of P is +3, it is necessary an oxidation and a deselenization to achieve the ligand precursor with the oxidation state +5.

As we can see in Scheme 22, the oxidative deselenization can be achieved using H_2O_2 and $BaCl_2 \cdot H_2O$ in dichloromethane at room temperature.

To prepare the P(III) precursor, the deselenization has to be carried out with a different path, since the oxidation of P(V) is not desiderable. This process consists in two steps, namely, the two-fold Se-methylation of the starting material using MeOTf and its consecutive treatment with $NaBH_4$ (Scheme 23).



Scheme 22. *Synthesis of [**J**(P^V)-H_2]$(Cl)_2$ via oxidative deselenization*

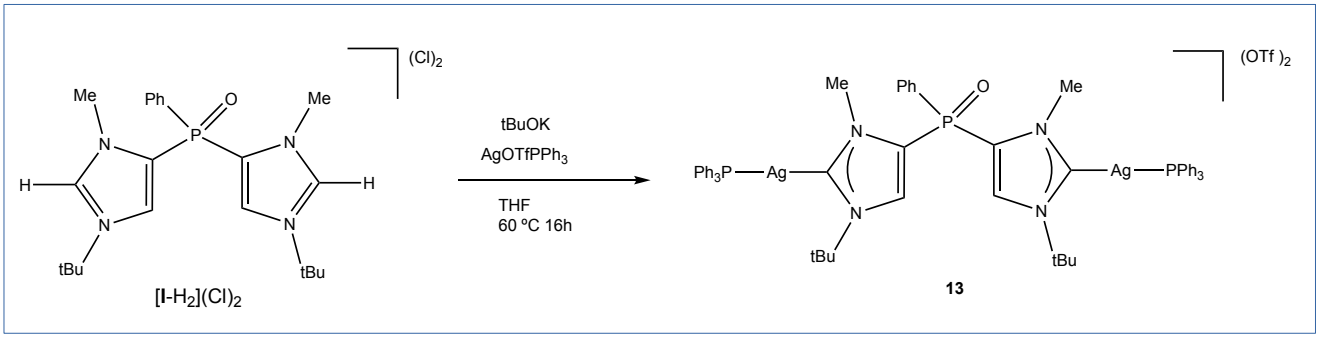


Scheme 23. *Synthesis of [**J**(P^{III})-H_2]$(OTf)_2$ via two fold Se-methylation and treatment with $NaBH_4$*

2.3.2 Metallic complexes and properties

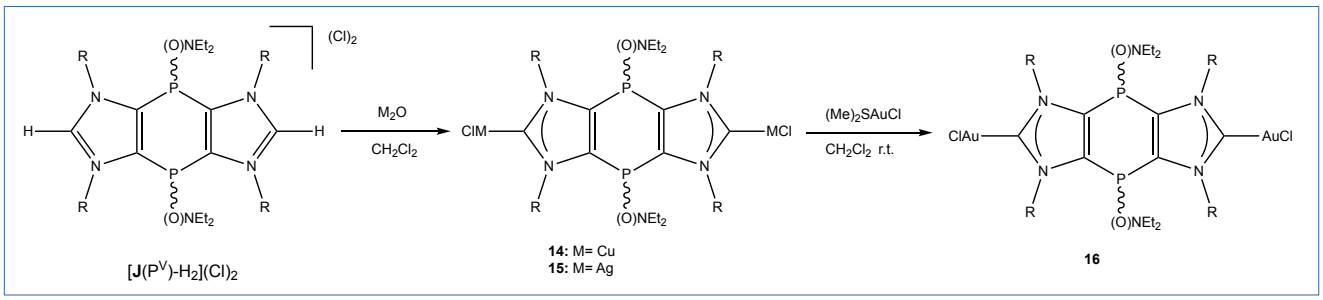
In this group, organometallic complexes have been studied, by binding these Janus-type ligands with the so-called coinage metals (Cu, Ag and Au).

In the case of the flexible ligand **I**, its precursor can be mixed with tBuOK and $AgOTfPPh_3$ in THF at 60ºC to obtain the silver bis(NHC) complex **13** (Scheme 24).



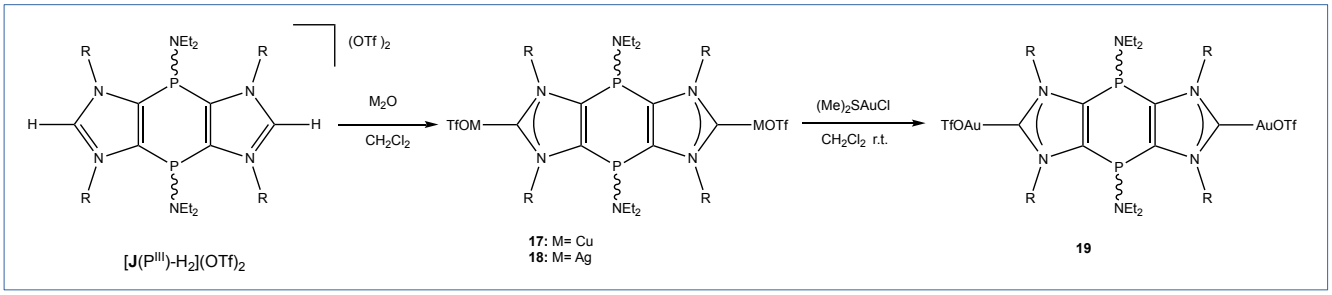
Scheme 24. *Synthesis of flexible silver P(V)-bridged complex **13** from [**H**-H_2]$(Cl)_2$*

The reaction of P(V)-bridged bis(imidazolium) salt precursor [**J**(P^V)-H_2]$(Cl)_2$ with either Cu_2O or Ag_2O in dichloromethane yielded linear complexes **14** and **15**, respectively. The transmetallation from Ag(I) complex **15** using $(Me)_2SAuCl$, allowed the isolation of complex **16**.



Scheme 25. *Synthesis of rigid P(V)-bridged bis(imidazolium) coinage metal (I) complexes*

Once having the P(III)-bridged bis(imidazolium) salt precursors [**J**(P^{III})-H_2]$(OTf)_2$, the synthesis of their coinage metal complexes is similar to that of its P(V) analogue (Scheme 26).



Scheme 26. *Synthesis of rigid P(III)-bridged bis(azolium) coinage metal (I) complexes*

The possibility to form rigid P(V)-bridged complexes in a similar procedure as that reported for the flexible P(V)-bridged complex **13,** might open the study to form flexible P(III)-bridged complexes with a similar path as the followed to obtain rigid P(III)-bridged complexes **17-19.**

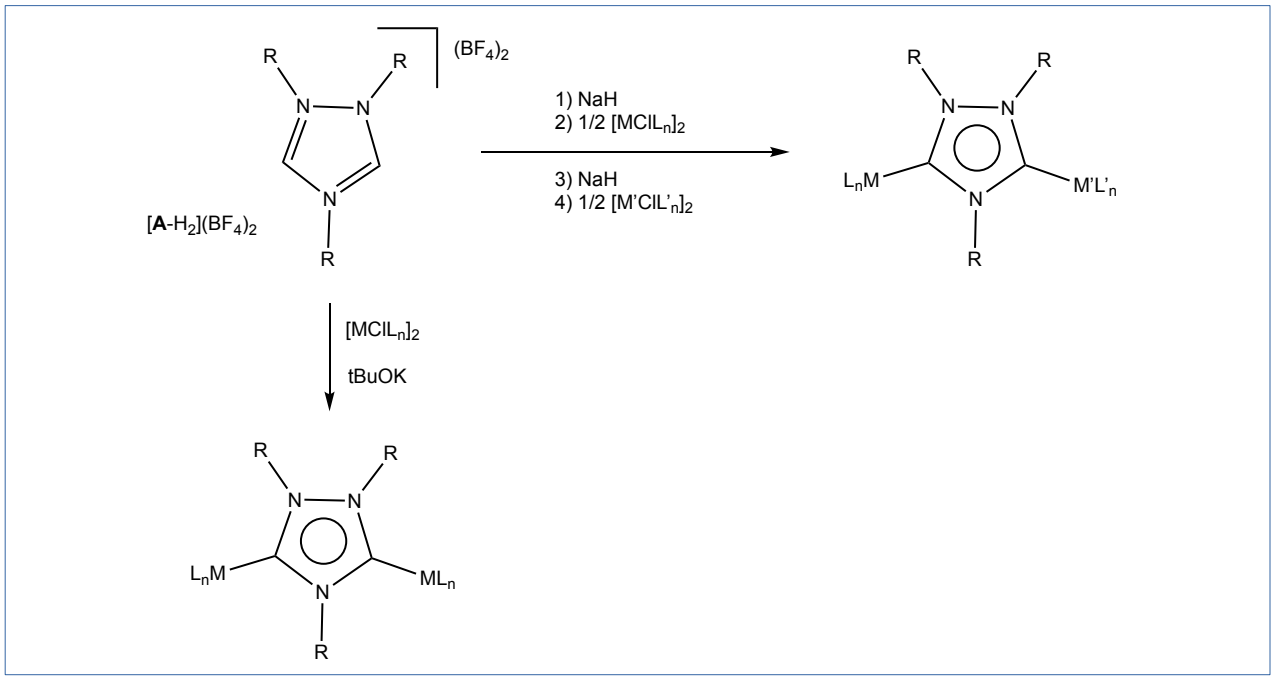
The different oxidation states of the phosphorous atom in these complexes make them interesting since it gives them the potential to participate in redox reactions and the different electronic properties may vary their catalytic properties.

3. Catalysis

As we mentioned in the introduction, NHCs have been widely used as ligands for classic organic transformations. In this regard, complexes based on with Janus-type bis-NHC ligands have advantages in this field thanks to their ability to bind to two (identical or different) metallic centers.

Even though there are many examples in the literature of complexes based on Janus-type bis-NHC ligands, their applications in catalysis are limited to those based on the so-called ditz ligand (**A** ligand in Scheme 1).

Ditz ligand has demonstrated to be able to coordinate to two identical metallic centers, forming homodimetallic complexes, as well as to two different metallic centers, forming heterodimetallic complexes[21,22] (Scheme 27).



Scheme 27. *Synthesis of homo- and heterodimetallic dizt-ligand-based complexes from [**A**-H_2](BF_4)$_2$*

This feature is very interesting, since it opened the possibility to use the heterodimetallic complexes as a catalyst in concatenated multistep processes, allowing the preparation of sophisticated molecules in one-pot synthesis. This is called a tandem process, in which each metal facilitates two or more mechanistically distinct cycles, that may be combined to compose the overall tandem process (Figure 9).

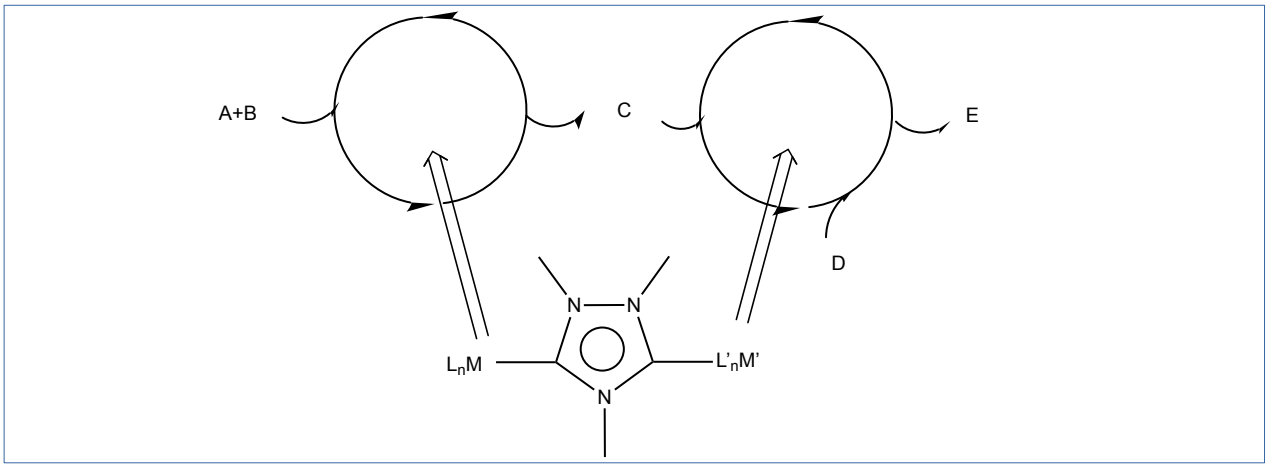
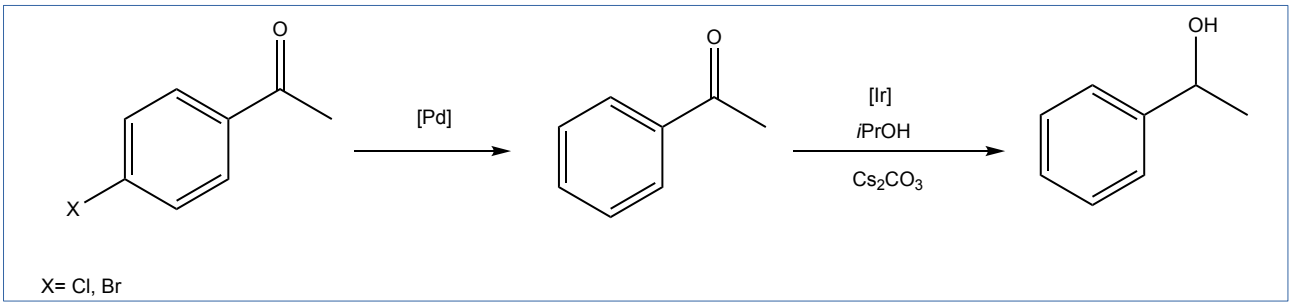


Figure 9. *Representation of a heterodimetallic complex catalyzing a tandem process*

The advantage of using this tandem application can be illustrated with the dehalogenation/transfer hydrogenation of haloacetophenone, where in the first step, the reaction is catalyzed by Pd(II) and the second step by Ir(III) (Scheme 28). Profs. Peris and Hahn demonstrated

in 2014 that using the heterodimetallic Ir(III)/Pd(II) complex **20** as catalyst provided better yields than using a mixture of the homodimetallic complexes of Ir(III) (**21**) and Pd(II) (**22**) (Figure 10)[22].



Scheme 28. *Dehalogenation/ transfer hydrogenation of haloacetophenone catalyzed by Pd(II) and Ir(III)*

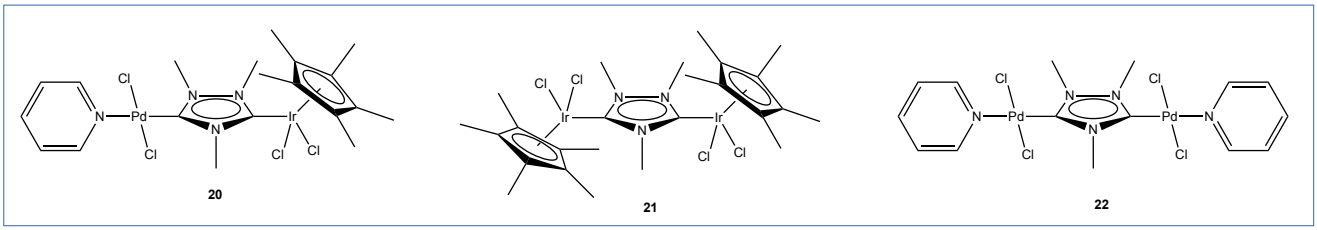
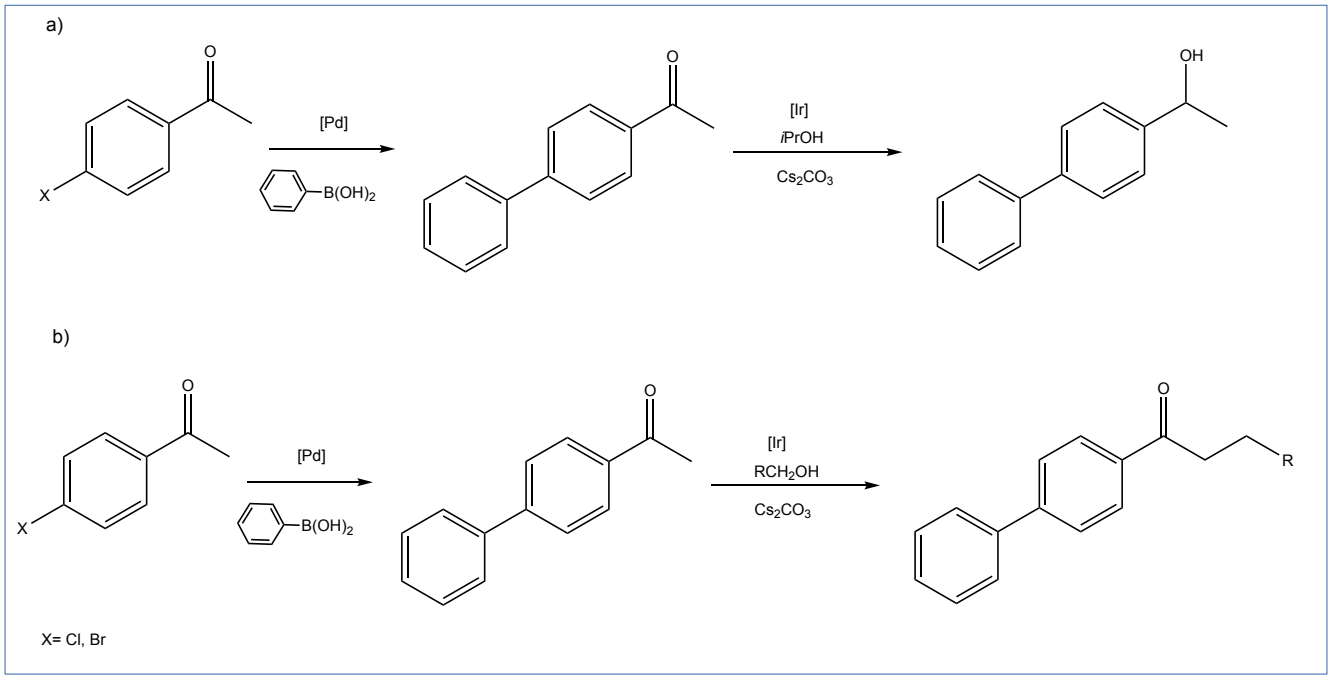


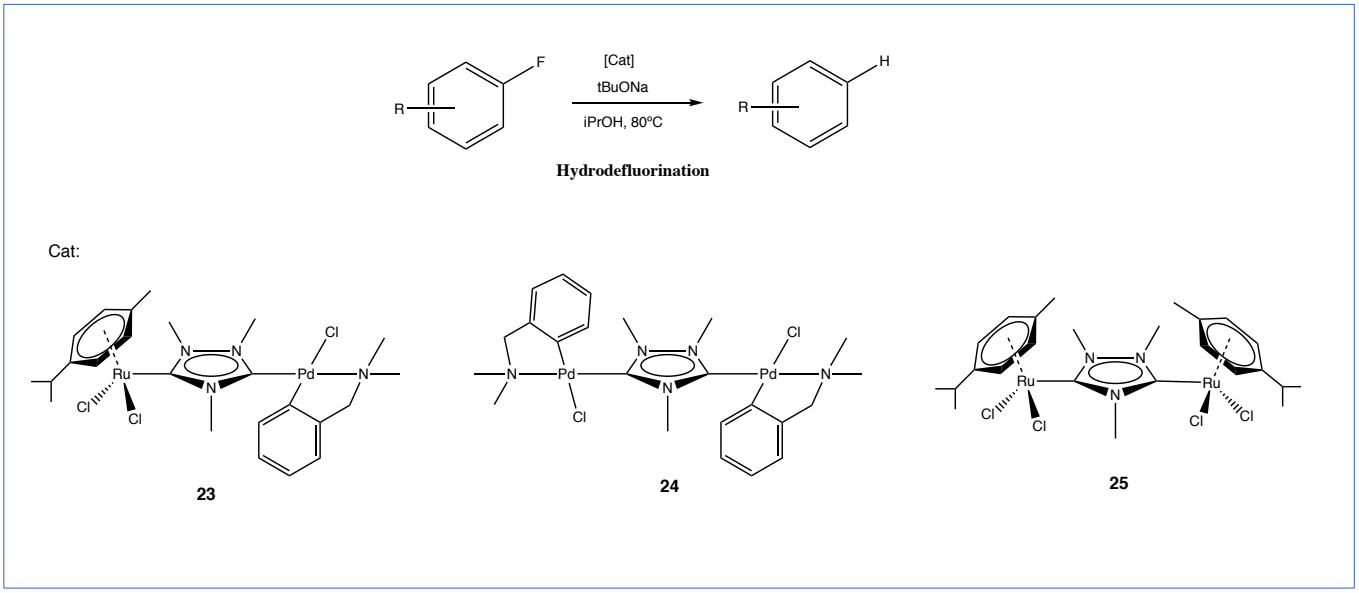
Figure 10. *Ditz-based Ir(III)/Pd(II) heterodimetallic complex and its homodimetallic counterparts*

Complex **20** also performed better than a mixture of complexes **21** and **22** in the tandem reactions depicted in Scheme 29, namely the Suzuki-Miyaura coupling/transfer hydrogenation and the Suzuki-Miyaura coupling/α-alkylation.



Scheme 29. *Examples of reactions catalyzed by heterodimetallic complex **20**: Suzuki-Miyaura coupling/transfer hydrogenation (a) and Suzuki Miyaura coupling/α-alkylation (b)*

In addition, it was demonstrated the advantage of using the different ditz-based heterodimetallic complexes over the mixture of its homodimetallic analogues in a variety of tandem processes such as the hydrodefluorination of a wide variety of fluoroarenes (Scheme 30). In these processes the heterodimetallic Pd(II)/Ru(II) complex **23** demonstrated to provide quantitative yields in short times and under mild conditions in contrast with the its homodimetallic counterparts, giving negligible yields when used separately and moderated yields when using a mixture[23]. This suggests that the two different metals have a role in the overall process, but also that the presence of these two metals in a single catalyst provides a significant benefit.



Scheme 30. *Hydrodefluorination of arenes catalyzed by ditz-based Ru(II)/Pd(II) heterodimetallic complex* ***23*** *and its homodimetallic counterparts*

4. Inter-metallic distance and supramolecular chemistry

As a result of the different topologies within the Janus-type bis-NHC we can obtain a variety of inter-metallic distances in the complexes formed with these ligands[10,14,24] (Figure 11).

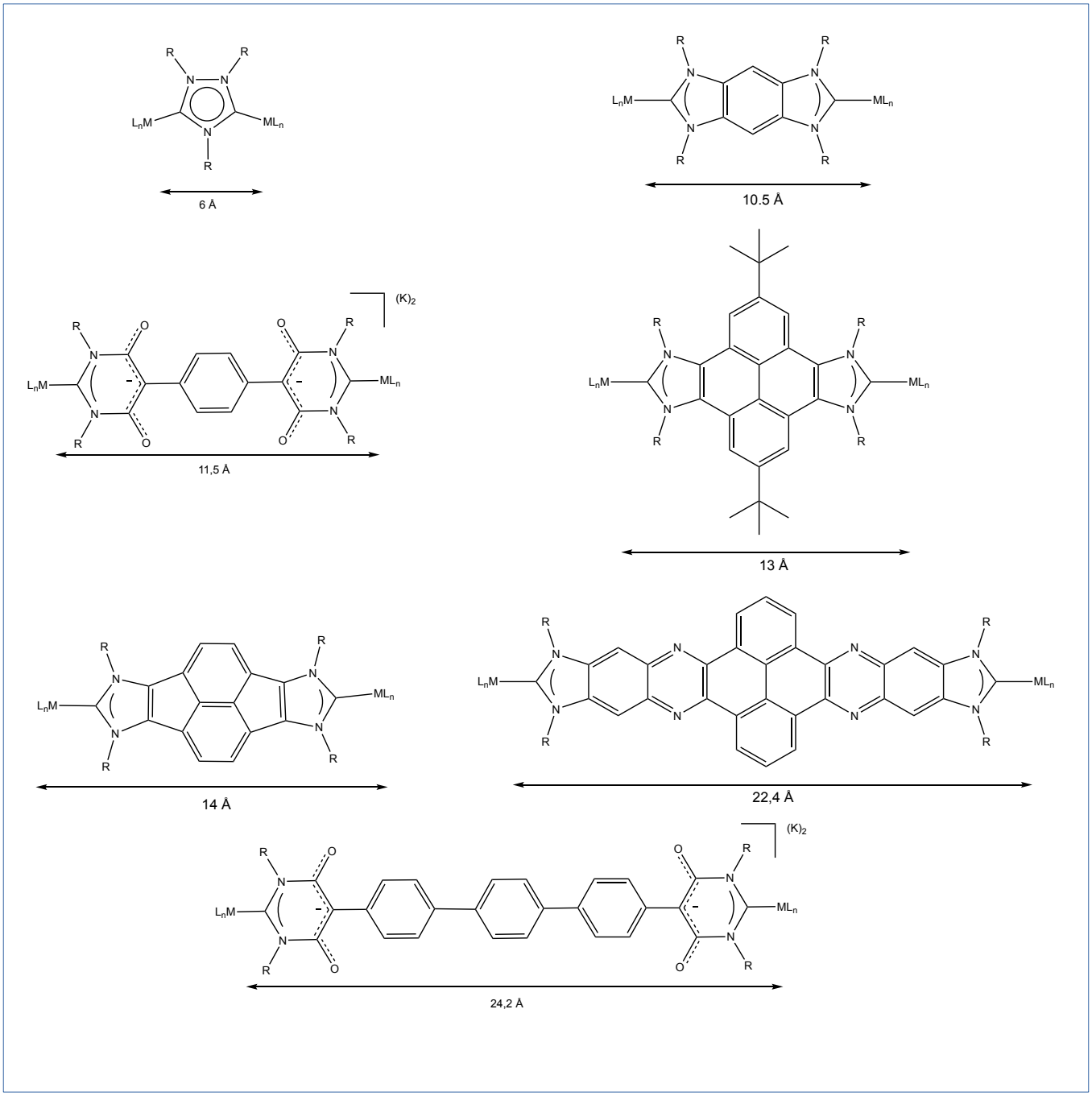


Figure 11. *Comparison of the inter-metallic distance in Janus-type ligands*

This property along the fact that the aromatic core provides rigidity to the molecule, can be useful when it comes to the supramolecular organometallic chemistry, making possible to build a variety of architectures with different sizes, from metallo-rectangles to metallo-cages, in which the size depends directly on the type of the Janus-type bis-NHC used to assemble them. In Figure 12 there is an example of a rectangular and square-shaped assemblies formed with ligand **B** and metals such as gold and nickel presented by Prof. Hahn's group[25,26].

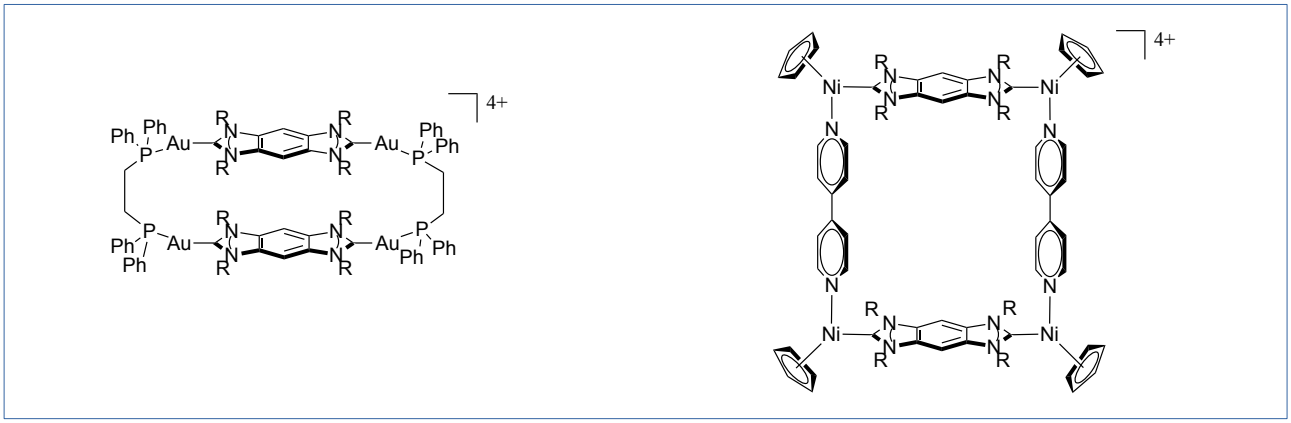


Figure 12. *Supramolecular assemblies presented by Prof. Hahn's group*

Figure 13 depicts a Au(I) complex designed by Prof. Peris and co-workers in which ligand **D** is being used as a building block for a square-shaped assembly. This assembly has shown to be very effective for the encapsulation of planar polycyclic aromatic hydrocarbons (PAHs) such as corannulene in CH_2Cl_2 [27].

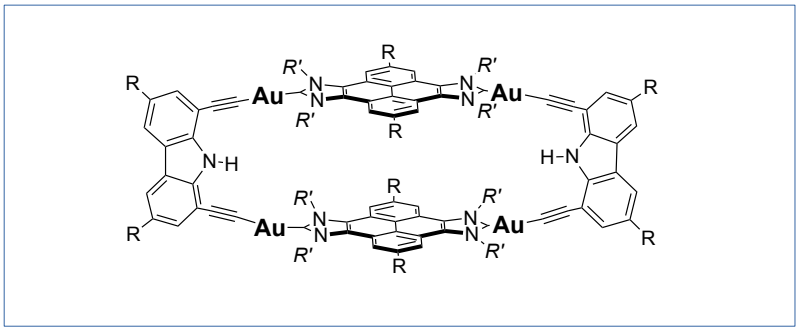


Figure 13. *Supramolecular square-shaped assembly presented by Prof. Peris*

5. Conclusions and future perspectives

The meteoric rise of bis-NHCs is far from arriving to its end. Janus-type bis-NHCs, from catalysis to the formation of polymers and supramolecular chemistry, are continuing to find new applications in organometallic chemistry.

The strength and stability of the metal-ligand bond as well as the ability to fine-tune the properties of organometallic complexes, through the structural modification of the ligand, gives Janus-type bis-NHCs a potential variety of topologies and applications only limited by the creativity and the will of the researcher. Their ability to coordinate with two different metallic centers, and to act as a catalyst in tandem processes open the gate to a more sustainable chemistry, reducing the quantity of catalyst needed to carry out organic processes.

Further studies may find new topologies of heterodimetallic complexes based in Janus-type bis-NHCs, and clear out their true catalytic potential, maybe changing the methodology of modern organic synthesis as we know it.

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